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February 29, 2012

Mr. Tien Q. Duong  
EE-2G/Forrestal Building  
Office of Vehicle Technologies  
U.S. Department of Energy  
1000 Independence Ave., S.W.  
Washington D.C. 20585

Dear Tien,

Here is the first quarter FY 2012 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://batt.lbl.gov/reports/quarterly-reports/>.

Sincerely,

Venkat Srinivasan  
Acting Head  
BATT Program

edited by: V. Battaglia  
M. Foure  
S. Lauer

cc:	J. Barnes	DOE/OVT
	P. Davis	DOE/OVT
	D. Howell	DOE/OVT
	J. Muhlestein	DOE-BSO

## ***FEATURED HIGHLIGHTS***

### ***Cell Analysis–***

- ✦ Chiang's Group fabricates electrodes that are greater than 200  $\mu\text{m}$  thick with rate capabilities of 2C.

### ***Anodes–***

- ✦ Kumta's, Zhang's, and Cui's Groups independently synthesize Si-composite nanostructures with excellent capacity retention with greater than 800 mAh/g reversible capacity.

### ***Electrolytes–***

- ✦ Bedrov and Borodin Group model predicts the stable configuration of the interfaces of  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ , which agrees with experiments, and can now be used to evaluate electrode/electrolyte reactions.

### ***Modeling–***

- ✦ Newman's Group shows that an electrolyte with  $\text{LiClO}_4$  forms a protective passive film on HOPG up to 3.7 V whereas an electrolyte of  $\text{LiPF}_6$  results in oxidative stripping of the SEI at 3.2 V.
- ✦ Srinivasan's Group accurately predicts cell discharge of an NCM electrode to 5C.

## **BATT TASK 1** **CELL ANALYSIS**

**TASK 1.1 - PI, INSTITUTION:** Vincent Battaglia, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Cell Analysis - Electrode Fabrication and Failure Analysis

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** High energy systems: low energy; moderate cycle life; moderate calendar life

**OBJECTIVES:** There are six overarching objectives associated with this task. 1) To bring fundamental understanding to the electrode fabrication process. 2) To make “good” electrodes and “good” cells. Good electrodes means electrodes that help identify chemical and physical limitations of a material, be it an active or inactive component. Good cells mean that the material is being evaluated in an environment consistent with what is found in a large size, industrially produced cell. 3) Determine the source or sources of electrode and cell failure and provide samples from used cells for diagnostics. 4) Provide a means for testing electrochemical models. 5) Provide a resource for others in the BATT program for making their own cells.

**GENERAL APPROACH:** These objectives are accomplished through methodically changing different aspects of the electrode fabrication process and examining the results of the changes *via* electrochemical, physical, and chemical characterization techniques. They are also carried out through close collaboration with other BATT PIs, publishing and speaking about all of our findings, and the willingness to share our resources and produce electrodes and cells as requested.

**STATUS OCT. 1, 2011:** Powders of LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> from NEI were distributed to interested PIs as well as an electrolyte of 1 M LiPF<sub>6</sub> in EC:DEC 1:2 from Daikin, America. After a large initial capacity loss in a full cell, the NEI high-voltage spinel material shows good cyclability. VC has a higher reduction potential than EC but with slower kinetics. Slow formation processes of cells with and without VC do not show significant differences in the rate of the side reactions.

**EXPECTED STATUS SEP. 30, 2012:** Differences in performance of a baseline electrolyte *versus* a “high-voltage” electrolyte against LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> will be elucidated. The effects of mixing time on electrode uniformity and performance will have been studied. The dissolution of spinel materials will be measured at 55°C.

**RELEVANT USABC GOALS:** PHEV-40: 207 Wh/l; 5000 deep-discharge cycles; 15 years.

### **MILESTONES:**

- (a) Measure the difference in performance of our baseline electrolyte when compared to a high voltage electrolyte from industry. (Dec. 11) **Complete**
- (b) Evaluate the effects of mixing time on cell performance. (Apr. 12) **On schedule**
- (c) Compare the rate of side reaction and capacity fade of Gr./NCM\* with and without VC. (Apr. 12) **On schedule**
- (d) Measure the rate of dissolution of a spinel material containing Mn. (Sep. 12) **On schedule**

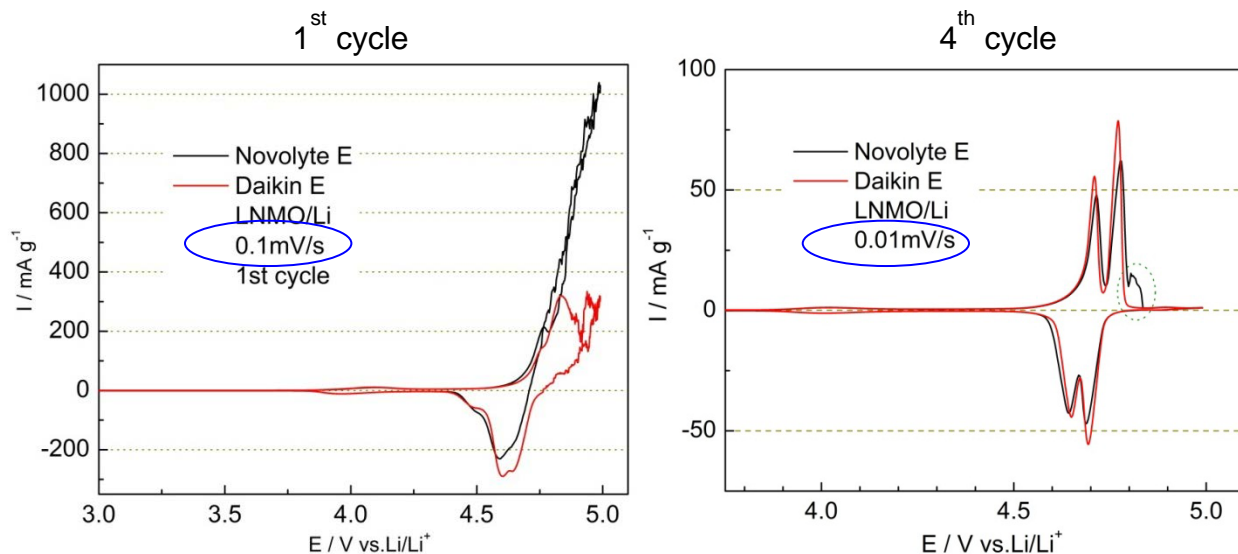
## PROGRESS TOWARD MILESTONES

- a) Measure the difference in performance of our baseline electrolyte when compared to a high voltage electrolyte from industry. Dec. 2011 **Complete**

Working with Daikin, America, it was agreed that they would distribute the 1 M  $\text{LiPF}_6$  in EC:DEC 1:2 baseline electrolyte directly to 10 PIs in the BATT Program, all of whom are participants in the  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  Focus Group. This was accomplished. EC:DEC 1:2 solvent has since been ordered to test different salts being developed within the Group. Previously in our possession was another popular source of electrolyte (A) of the same composition. The two electrolytes were tested in half-cells of Ni-spinel cathodes made from the same laminate.

The figures below are of the cyclic voltammograms (CVs) of each electrolyte performed on fresh cells. The figure on the left is of the first cycle at a sweep rate of  $0.1 \text{ mVs}^{-1}$ . If the majority of the capacity is within a 200 mV window, than this sweep rate is equivalent to a galvanic charge and discharge of 2C. One sees that at this high rate, the side reaction of the cell with the Novolyte electrolyte is greater than the rate of intercalation between 4.85 and 5 V. A side reaction is seen with the Daikin electrolyte in the same voltage range but a factor of 4 less. After the first cycle, the side reaction was significantly suppressed and the two cells performed similarly (not shown).

The figure on the right is of the 4<sup>th</sup> CV where the voltage sweep rate was reduced by an order of magnitude to  $0.01 \text{ mVs}^{-1}$ . At this lower rate it was possible to capture small differences between the two electrolytes. One sees that the peaks on charge and discharge for the Daikin electrolyte are sharper and there still remains a small signature above 4.8 V for the Novolyte electrolyte.



- b) Evaluate the effects of mixing time on cell performance; April 2012 **On schedule**  
 c) Compare the rate of side reaction and capacity fade of Gr./NCM with and without VC. April 2011 **On schedule**  
 d) Measure the rate of dissolution of a spinel material containing Mn; Sept 2012 **On schedule**

**TASK 1.2 - PI, INSTITUTION:** Thomas Richardson, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Analysis - Cell and Component Diagnostics

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000cycles/58 MWh).

**OBJECTIVES:** Investigate the relationship of structure, morphology and performance of cathode and anode materials. Explore kinetic barriers, and utilize the knowledge gained to design and develop cells with improved energy density, rate performance and stability.

**GENERAL APPROACH:** Employ XRD, visible and electron microscopy, vibrational spectroscopies, and electro-analytical techniques to determine their applicability to BATT goals. Characterize known and modified electrode materials and establish correlations between performance and factors such as crystal structures, morphologies, and surface chemistry. Provide guidelines for materials synthesis and electrode fabrication processes.

**STATUS OCT. 1, 2011:** To have developed new techniques for visualizing the distributions of both materials and charge in lithium battery electrodes. These have been applied to LFP cathodes.

**EXPECTED STATUS SEP. 30, 2012:** Additional methods will have been demonstrated for diagnosis and evaluation of cell components. Charge distribution diagnostics will have been applied to electrodes harvested from commercial cells.

**RELEVANT USABC GOALS:** 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

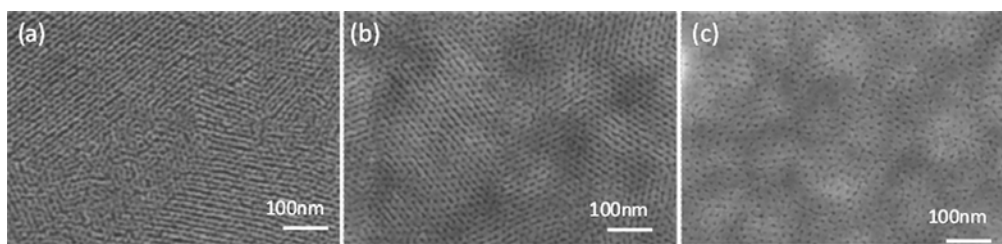
**MILESTONES:**

- (a) Complete charge distribution assessments of harvested cathodes. (Mar. 12) **On schedule**
- (b) Develop new optical microscopy methods for *in situ* and *ex situ* diagnosis of electrode and separator chemistries. (Aug. 12) **On schedule**

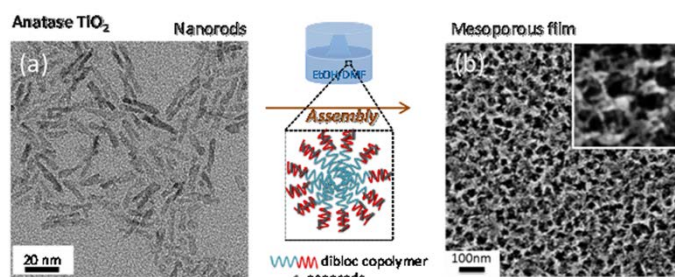
## PROGRESS TOWARD MILESTONES

The influence of electrode composition and structure on performance, especially at high charge-discharge rates is of considerable importance for both high power and high energy batteries. Improved utilization of active material and reduction of electrochemical stress by maximizing the uniformity of the current distribution can increase capacity and extend cell life. Methods developed in the BATT Program have been applied to visualize charge distribution in cathodes using spatially resolved x-ray diffraction (XRD) and by creating 3D images of electrodes by focused ion beam (FIB) tomography... These techniques revealing the sizes, shapes and spatial distribution of the active material, conductive additives, binder, voids and cracks. Further, we have begun a collaboration with Dr. Vassilia Zorba of LBNL to analyze and map charge distribution using ultrafast laser induced breakdown spectroscopy (LIBS). This technique offers elemental analysis with high spatial resolution, is ideal for depth profiling, and, unlike most other techniques, is especially sensitive to lithium. A commercial 18650 nanophosphate cell was disassembled in a discharged state, and the electrodes and separator removed. Following in-plane mapping of the harvested electrodes, smaller pieces will be incorporated in coin and pouch cells for further mapping after cycling at different rates and in a variety of configurations.

Porosity plays a crucial, but poorly quantified role in electrode performance. Composite electrodes, consisting of randomly packed active particles with carbon and binder, are extremely complex, presenting a variety of pore sizes and interconnections. We are studying model electrodes consisting of mesoporous thin films (MTFs) of anatase  $\text{TiO}_2$  with uniform pore sizes and wall thicknesses. They were prepared by evaporation-induced self-assembly from an inorganic precursor and spheres of an amphiphilic diblock copolymer (Fig. 1), and from  $\text{TiO}_2$  nanorods with well-defined size, shape and crystallinity. They were then assembled into MTFs by exploiting specific interactions between the block copolymers and the nanocrystal surfaces (Fig. 2). The pore structures strongly influence their electrochemical behavior.



**Figure 1.**  $\text{TiO}_2$  MTFs with 7 nm pores and dense walls (a) 7 nm, (b) 9 nm and (c) 16 nm in thickness.



**Figure 2.**  $\text{TiO}_2$  MTFs starting from nanorods.

**Collaborations:** Robert Kostecki, Guoying Chen, Marca Doeff, Venkat Srinivasan, Jordi Cabana, Vince Battaglia, the Molecular Foundry, National Center for Electron Microscopy, Advanced Light Source and Stanford Synchrotron Radiation Laboratory.

**TASK 1.3 - PI, INSTITUTION:** K. Zaghib, Hydro-Québec (IREQ)

**TASK TITLE PROJECT:** Cell Analysis - Interfacial Processes- SEI Formation and Stability on Cycling

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy and poor cycle/calendar life

**OBJECTIVES:** Synthesis and evaluation of high voltage cathode (spinel Mn-Ni) with improved electrochemical stability. Reduce the oxidation of the cathode composition, electrolyte, and separator. Find the appropriate alternative anode material composition that meets the requirement for low cost and high energy. Continue the development of binders for the cathode and alternative anode to understand and improve the properties of the SEI layer.

**GENERAL APPROACH:** Our approach is to develop an appropriate method to stabilize the interface reaction of the high voltage oxide (Mn-Ni based like LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>) by surface coating with more stable material like olivine. The emphasis is to improve electrochemical performance at high voltage. Binder type, electrolyte composition, separator will be investigated at this level of voltage. Going with high capacity anode; Si based anode composition will be optimized in terms of particle size (micro vs. nano), graphite and SiOx content.

**STATUS OCT. 1, 2011:** Effort is oriented to silicon based anode alloys; LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> based cathode and SEI study and its stabilization. Work will start on these items in August by exploring an appropriate composition of anode material based on carbon coated nano-silicon, SiOx and graphite. More work on high voltage cathode will be addressed by reducing its oxidation problem with electrolyte.

**EXPECTED STATUS SEP. 30, 2012:** Due to its low cost and high capacity, the development of silicon-oxide anodes material will continue to achieve the DOE objectives, research will be conducted to find a suitable composition of the Si-based high capacity anode. Different anode composition; pure Si and its mixing with SiOx and graphite will be investigated. For the cathode side, as recommended by the DOE, high voltage cathode based on Mn-Ni spinel oxide will be used in this work. In order to reduce the oxidation of the electrolyte at high voltage, some items will be considered; more stable binder, different electrolyte composition, carbon additives and surface coating of this high voltage cathode. With the scope of the work tendency, the investigation of SEI layer on both sides of the anode and cathode is essential. Many parameters will affect this SEI layer; binder type, electrolyte composition, the cathode and anode composition.

**RELEVANT USABC GOALS:** High energy and low cost: 96 Wh/kg (PHEV, 40 miles). Cycle life, calendar life: 15 year life (at 40°C).

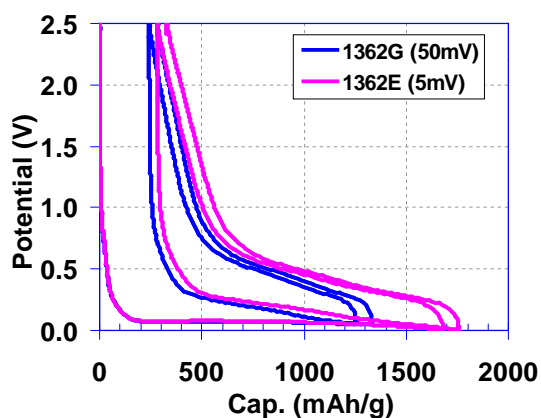
**MILESTONES:**

- (a) Identify a candidate of a silicon based composition as anode material (Mar. 12) **On schedule**
- (b) Demonstrate stabilized high-voltage LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> spinel cathode material with surface-coated of ceramic and oxides material (Sep. 12) **On schedule**
- (c) Complete the development the *in situ* SEM analysis of the Si-based anode (Sep. 12) **On schedule**

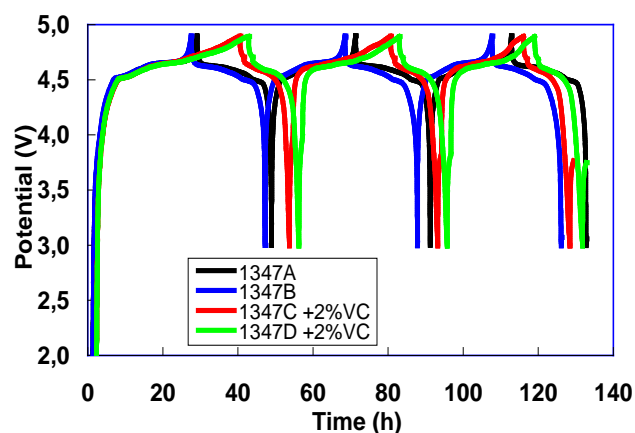


## PROGRESS TOWARD MILESTONES

In order to develop anode alloys operating at 1200 mAh/g and higher, Si-based materials should be considered; optimization of anode configurations is an active area of research. The challenges are to reduce the volume expansion and increase the first-cycle coulombic efficiency. From our recent work with alloy materials, in particular, mixtures of C-SiO<sub>x</sub> with graphite, a maximum capacity of *ca.* 900 mAh/g was achieved with a composition of graphite:C-SiO<sub>x</sub> of 1:1. Our studies of the effect of the binder on the Si composite electrode have included the polymers PVDF, SBR, polyimide, and EPDM. Currently, our investigation on a new binder has extended to those of an “Alginate” origin. By using this binder, a water based solvent is used (which should reduce cost). The anode was evaluated in Li-cells with EC-DEC-1M LiPF<sub>6</sub>; the discharge voltage was set at 5 mV or 50 mV. The result of the first cycles is shown in Fig.1. Reversible capacities of 1427 and 1048 mAh/g were obtained respectively for the 5 and 50 mV cut-off voltages. In the first-cycle coulombic efficiency (CE1) was found higher for the cell discharged to 50 mV (83.2%) as compared to the 80.6% for the discharges to 5 mV. The CEs in the second cycle were comparable at 96.5%. By using the new binder, the EC1 was improved - higher than the 80% that was obtained with a polyimide heated to 150°C. The measurement of the cycle life of this anode is in progress.



**Figure 1.** Li/C-SiO<sub>x</sub> and fully discharged to 5 and 50mV cut off voltages in EC-DEC-1M LiPF<sub>6</sub>.



**Figure 2.** First few cycles of LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>/Graphite in EC-DEC-LiPF<sub>6</sub> with VC and without VC.

The influence of 2% vinyl carbonate (VC) additive and anode composition were investigated with the high-voltage-spinel cathode material (LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>). The Li metal was replaced with graphite and assembled Li-ion cells with and without 2% VC added to EC-DEC-1M LiPF<sub>6</sub>. The first formation cycles at C/24 in Fig. 2 show clearly the effect of VC on the charging plateau. A side reaction from VC occurs during oxidation at 4.8 to 4.9 V. The reversible capacity with VC was 83 mAh/g compared to 130 mA/g when VC was absent. The first/second coulombic efficiencies are 32%/46% and 75%/91% for cells with and without VC, respectively. Furthermore, by replacing the Li metal with a graphite electrode, an instability that appeared in the high-voltage plateau was eliminated; this could be associated with some oxidized species that affects the Li surface. Further analysis will be performed to understand the effect of VC degradation on the LMNO cathode material.

HQ is continuing collaborations with LBNL researchers in the BATT Program, Vince Battaglia and Robert Kostecki.



**TASK 1.4 - PI, INSTITUTION:** Yet-Ming Chiang, Massachusetts Institute of Technology

**TASK TITLE - PROJECT:** Cell Analysis – New Electrode Design for Ultrahigh Energy Density

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** High energy system: low energy, poor cycle life

**OBJECTIVES:** Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology for a range of electrode-active materials. Characterize transport properties in high voltage Ni-Mn spinel.

**GENERAL APPROACH:** Fabricate high density sintered cathodes and anodes with controlled pore volume fraction and pore topology. Electrochemically test electrodes in laboratory half-cells and small lithium ion cells (<100 mAh), and model electrode response. Aim to increase cell-level specific energy and energy density by maximizing electrode density and thickness, under operating conditions commensurate with USABC targets for PHEV and EV. Titrate Li content in pure single phase sintered porous electrodes while measuring electronic and ionic transport.

**STATUS OCT. 1, 2011:** 1) Fabrication and testing of at least two cathode materials in the proposed high density low tortuosity electrode approach; 2) Development of methodology for measurement of electronic conductivity vs. Li concentration in porous sintered electrodes.

**EXPECTED STATUS SEP. 30, 2012:** 1) Conclude electrode fabrication and electrochemical testing in at least one targeted cathode compound; 2) Fabrication and testing of high density low tortuosity electrodes of at least one anode compound; 3) Conclude measurement of electronic conductivity vs.  $x$  in sintered undoped Li <sub>$x$</sub> Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

**RELEVANT USABC GOALS:** EV: 200 Wh/kg; 1000 cycles (80% DoD).

**MILESTONES:**

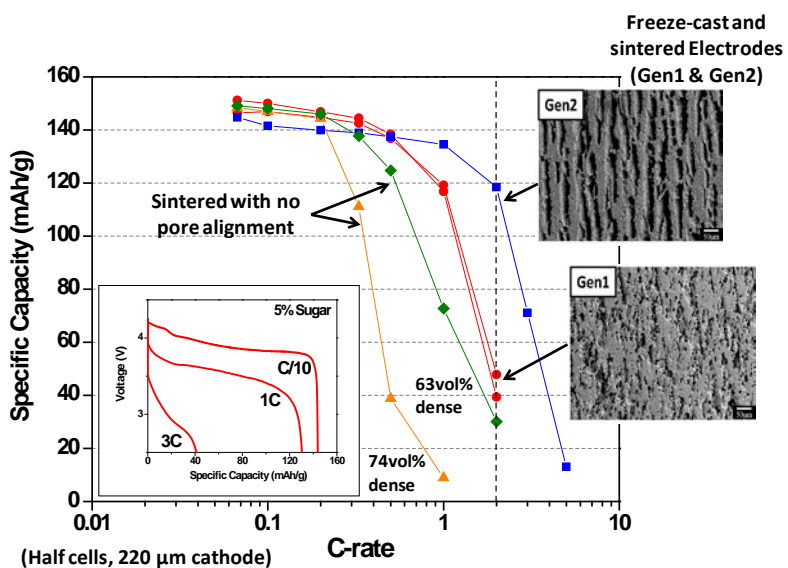
- (a) Demonstrate >80% capacity retention at 2C rate in additive-free low tortuosity LiCoO<sub>2</sub> electrode of >50 vol% density and >200  $\mu$ m thickness. (Oct. 11) **Complete**
- (b) Complete measurement of electronic conductivity vs.  $x$  in sintered undoped Li <sub>$x$</sub> Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>. (Jan. 12) **On schedule**
- (c) Complete measurement of electronic conductivity vs.  $x$  in sintered Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode. (Jan. 12)
- (d) Develop tortuosity measurement for freeze-cast/sintered cathodes. (Mar. 12) **On schedule**
- (e) Complete process development study for directionally freeze-cast and sintered LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathodes. (Jun. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

Collaborator: Antoni P. Tomsia (LBNL)

**Accomplishments:** During the current reporting period, the milestone of demonstrating >80% capacity retention at 2C rate in additive-free low tortuosity  $\text{LiCoO}_2$  electrode of >50 vol% density and >200  $\mu\text{m}$  thickness was met. The significance of this milestone is that it demonstrates electric vehicle-capable discharge rates in cathodes having approximately twice the thickness and twice the areal capacity of current Li-ion electrodes. The electrodes tested were produced by directional freeze-casting of aqueous  $\text{LiCoO}_2$  powder suspensions followed by sintering, a process for which the procedures and resulting electrode microstructures have been reported previously. An example of electrochemical testing results for freeze-cast  $\text{LiCoO}_2$  samples is shown in the figure. Here, capacity utilization vs. C-rate of the freeze-cast microstructures is compared with that for sintered electrodes without the aligned low-tortuosity pore features. At low C-rates (C/10) the specific capacity of all samples are similar. With increasing C-rate, however, the results diverge significantly. Comparing at 1C rate, the Gen 1 sample, which has aligned porosity due to freeze-casting (although not as high a degree of alignment as Gen 2), shows significant increase in capacity over both of the sintered samples (at 63 and 74% dense), retaining ~83% (120 mAh/g) of the low-rate capacity. The Gen 2 sample, which has highly-aligned pores (and somewhat lower sintered density of 50%), shows further improved capacity retention, with the same capacity achieved at 2C as for the Gen1 at 1C. Thus, these results validate the approach of introducing low tortuosity porosity to improve rate capability at high electrode densities.

In addition, progress was made this quarter towards upcoming milestones in which the electronic conductivity of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  will be reported as a function of lithiation; work conducted as part of the BATT Focus Group on high voltage Ni-Mn spinels. These transport measurements are also being conducted using the additive-free, sintered electrode format to allow facile electrochemical titration of Li content and simultaneous electrical measurement. In parallel, the electronic conductivity vs. Li content in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel is being measured for the first time. This is a useful testbed material for the present approach due to its “zero-strain” properties, as well as an anode material of much interest in its own right for high-power and long-life Li-ion systems.



**TASK 1.5 - PI, INSTITUTION:** Gao Liu, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Analysis - Advanced Binder for Electrode Materials

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** High energy system: poor cycle life, high first cycle irreversible capacity, low coulomb efficiency.

**OBJECTIVES:** Develop new conductive polymer binder materials to enable large volume change lithium storage materials to be used in lithium-ion electrode.

**GENERAL APPROACH:** Use functional polymer design and synthesis to develop new conductive polymers with proper electronic properties, strong adhesion and improved flexibility to provide electric pathways in the electrode, and to accommodate large volume/phase change of the active material during lithium insertion and removal.

**STATUS OCT. 1, 2011:** Gained fundamental understanding of the Si particle surface properties to the electrode performance characteristics; developed HF etching process to clean off SiO<sub>2</sub> surface layer for improved initial performance; demonstrated change of porosity of the cycled Si/conductive polymer electrode as a main issue to prevent high loading electrode from stable cycling, demonstrated over 600 cycles of the Si/conductive polymer composite electrode between 0.01-1V vs. Li/Li<sup>+</sup> with less than 15% capacity loss, and demonstrated initial cycling performance of the Sn/conductive binder electrode.

**EXPECTED STATUS SEP. 30, 2012:** Investigate conductive binder properties to Si electrode performance in various electrode compositions and configurations; explore electrolyte and additives to increase coulomb efficiency; and explore the conductive binders in other high capacity material systems.

**RELEVANT USABC GOALS:** PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

**MILESTONES:**

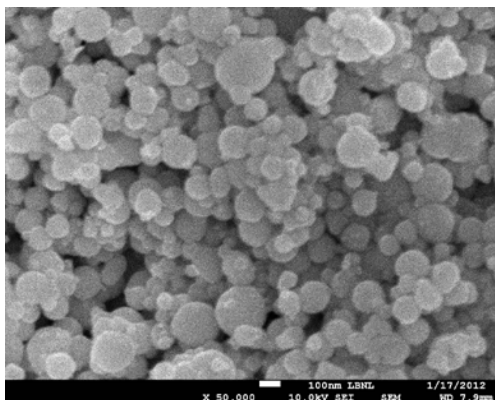
- (a) Continue to optimize the Sn/conductive binder electrode system to achieve 600 mAh/g-Sn specific capacity cycling. (Mar.12) **On schedule**
- (b) Study conductive binder properties to Si electrode performance in various electrode compositions and configurations, aim to achieve 3.5 mAh/cm<sup>2</sup> loading electrode. (Sep. 12) **On schedule**
- (c) Develop one type of electrolyte additives and select Si materials to minimize side reactions, and increase coulombic efficiency to 99.5%. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

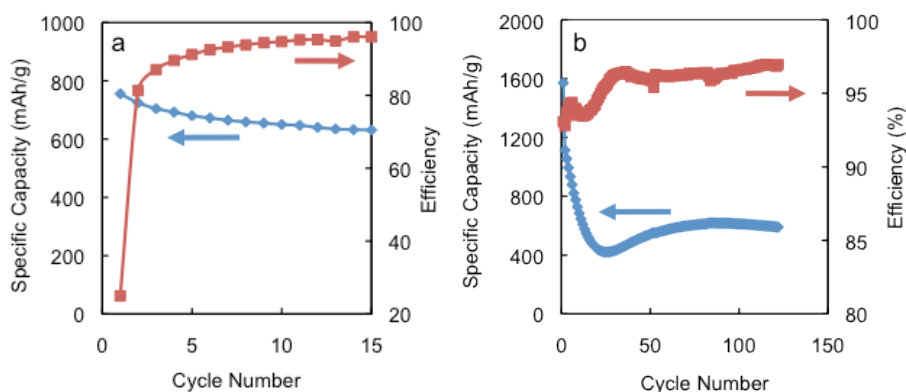
The Si anode-based electronically-conductive binder PFFOMB [1] had been designed and synthesized in the past years. The polymer binder belongs to a class of polyfluorene conductive polymers. The superb stability of this binder was demonstrated through extensive cycling of the Si/conductive polymer composite electrode. This polymer binder can be equally applicable to the Sn-based anode, which also has volume change issue during a Li insertion and removal process.

Figure 1 is the SEM image of the Aldrich commercial Sn nanoparticles. The average particle size is around 100 nm. The particle size distribution is more uniform compared to the CVD nano Si particles. Figure 2a demonstrates the cycling performance of the PFFOMB binder in combination with a 100 nm commercial available Sn nanoparticles. The reversible capacity is around 600 mAh/g of Sn. The Sn nanoparticles are also covered with a layer of  $\text{SnO}_2$ , which causes the very large first cycled irreversible capacity change. The discharge capacity of the PFFOMB binder based Sn electrode was stable over 15 cycles against Li-metal electrode. In this electrode system, acetylene black (AB) must be used in the formulation for the Sn to cycle.

By comparison, the Sn particles were made into an electrode with PVDF and acetylene black. This composite electrode was tested at similar conditions as the PFFOMB system. The capacity retention was very different for the two electrodes (Fig. 2). The cycling efficiency of the PFFOMB electrode was significantly better than the PVDF electrode, suggesting some sort of surface stability is provided by the PFFOMB electro-conductive binders.



**Figure 1.** SEM image of the Aldrich Sn nanoparticles.



**Figure 2.** Cycling behavior of the Sn based electrodes. a. Sn/PFFOMB/AB; b. Sn/PVDF/AB.

**Publication:** G. Liu, H. Zheng, X. Song, and V.S. Battaglia, "Particles and Polymer Binder Interaction: A Controlling Factor in Lithium-Ion Electrode Performance," *J. Electrochem. Soc.*, **159**, A214 (2012).

[1] PFFOMB stands for Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester)..

**TASK 1.6 - PI, INSTITUTION:** Guoying Chen, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Analysis - High-Energy Cathodes - Improving Performance, Safety, and Cycle Life through Structure and Morphology Design

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000 cycles/58 MWh).

**OBJECTIVES:** Identify phase transition mechanisms and kinetic barriers of high voltage and high capacity cathode materials. Establish direct correlations between crystal structure, composition, morphology, performance and stability. Provide guidelines to design and fabricate cathode materials with improved energy density, rate capability and safety, especially with regard to thermal stability.

**GENERAL APPROACH:** Prepare well-formed crystals with various structure, composition, size and morphology using wet synthesis routes, such as solvothermal and molten salt methods. Characterize their physical properties and investigate their solid state chemistry using advanced spectroscopic, spectromicroscopic, scanning calorimetry and electron microscopic techniques.

**STATUS OCT. 1, 2011:** Overlithiation in Li<sub>1+x</sub>(Ni<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>)<sub>1-x</sub>O<sub>2</sub> (NMC333) was found to increase extractable Li in the structure and energy density of the cathode. Increasing Mn content in the overlithiated NMC333 improves rate capability but decreases the stability of the initial O3 phase, which transforms to P3 structure upon deep Li extraction. The irreversible charging plateau observed at high voltage was attributed to overlithiation in Li<sub>1+x</sub>M<sub>1-x</sub>O<sub>2</sub>. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> single crystals were synthesized in a variety of sizes and shapes, with the best performance achieved with the octahedral micron-sized crystals. Large crystals with a range of Mn<sup>3+</sup> content were prepared by varying the Ni/Mn ratio in LiNi<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub>. Synthesis precursors were found to influence the transition-metal ordering in the prepared spinel.

**EXPECTED STATUS SEP. 30, 2012:** The effect of structural, composition and morphological changes during Li extraction and insertion in Li<sub>1+x</sub>M<sub>1-x</sub>O<sub>2</sub> will have been further evaluated. Oxygen evolution mechanism and kinetics will have been investigated. The effect of particle size and morphology on oxide activation process and electrode stability will have been revealed. The impact of Mn<sup>3+</sup> content on property and performance of LiNi<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> cathode will have been established, and the kinetics of structural disordering in the spinel examined.

**RELEVANT USABC GOALS:** PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD)

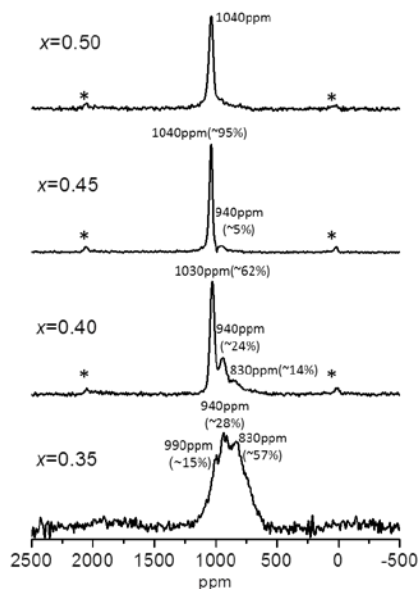
**MILESTONES:**

- (a) Investigate the kinetics of order/disorder transitions in LiNi<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub>. (Mar. 12) **On schedule**
- (b) Determine the effect of Mn<sup>3+</sup> content on property and performance of the spinels. (Jun. 12) **On schedule**
- (c) Investigate the mechanism and kinetics of delithiation/relithiation on oxide crystals. (Aug. 12) **On schedule**
- (d) Synthesize at least four oxide crystal samples with different physical characteristics. (Sep. 12) **On schedule**

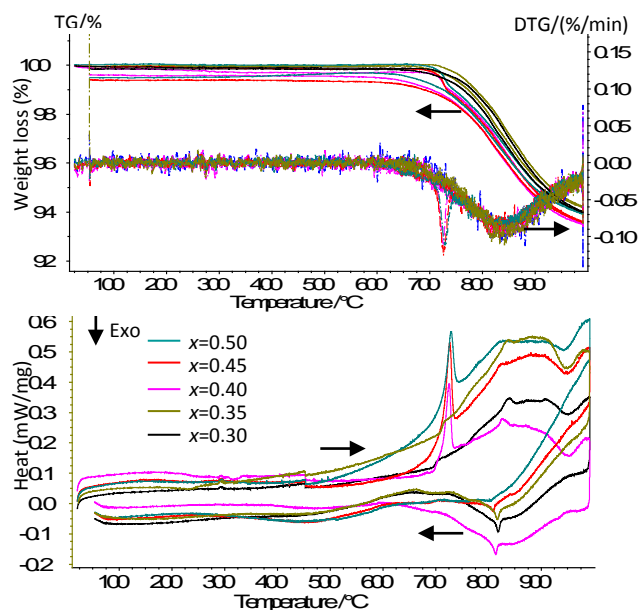
## PROGRESS TOWARD MILESTONES

**Ni/Mn Spinel:** Our previous report demonstrated that FTIR is a useful qualitative technique to measure transition-metal ordering in spinel structures. Detailed analysis of the  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  ( $0.3 \leq x \leq 0.5$ ) spectra showed that while samples with higher Ni content were mostly ordered, an abrupt loss of ordering occurred at Ni contents below 0.35. In collaboration with Grey's group, the changes in the ordering scheme within the series were corroborated by  $^6\text{Li}$  MAS NMR. The broad resonance with peaks at 830, 940, and 990 ppm for the sample with a Ni content of 0.35 suggests a disordered structure, as shown in Fig. 1. Increasing the Ni content quickly reduced the line width and intensity of the peaks at low frequencies, with the spectrum at  $x=0.5$  having a single peak at 1040 ppm. The results also suggest that the octahedron-shaped  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  single crystals are nearly perfectly ordered.

The effects of  $\text{Mn}^{3+}$  content and structural ordering were further investigated by thermal analysis. In a simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) instrument, the  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  series were heated and then cooled in air at a rate of  $3^\circ\text{C}/\text{min}$ . As shown Fig. 2a, the total weight loss on heating to  $1000^\circ\text{C}$  ranged from 5.8 to 6.5%, depending on the  $\text{Mn}^{3+}$  content in the samples. The broad reversible peaks that developed at  $700^\circ\text{C}$  and centered at  $830^\circ\text{C}$  on the differential TGA traces were attributed to the loss of oxygen. For the ordered samples with Ni content above 0.35, an additional peak corresponding to structural disordering was observed at  $720^\circ\text{C}$ . This suggests that disordering is promoted by the initial reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  and oxygen loss. In the DSC traces (Fig. 2b), the sharp endothermic peaks at  $720^\circ\text{C}$  suggest that disordering is a first order transition. The reversible peaks at  $810^\circ\text{C}$  are likely due to the extrusion and incorporation of the rock salt phase,  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , during heating and cooling, respectively. The loss of oxygen between 700 to  $950^\circ\text{C}$  was further revealed as the broad peaks on the DSC profiles. Additional investigations into the possible reordering and the initial  $\text{Mn}^{3+}$  content in the spinel samples will be performed with slower scan rates and controlled atmospheres.



**Figure 1.**  $^6\text{Li}$  MAS NMR of  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  crystals.



**Figure 2.** a) TGA and b) DSC profiles of  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  crystals.

**Collaborations this quarter:** Richardson, Grey, Angell, Cabana, Kostecki, Doeff, Chiang, SSRL, NCEM.

## **BATT TASK 2**

### **ANODES**

**Task 2.1-PI, INSTITUTION:** Jack Vaughey, Argonne National Laboratory

**TASK TITLE:** Anodes: Novel Anode Materials

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy, poor low-temperature operation, and abuse tolerance limitations

**OBJECTIVES:** To address and overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes by designing electrode architectures containing main group metal, metalloid or intermetallic components that can tolerate the volumetric expansion of the materials and provide an acceptable cycle life.

**GENERAL APPROACH:** Our approach is to search for anode materials or formulations that provide an electrochemical potential a few hundred mV above the potential of metallic Li. Effort will be predominantly on Sn- and Si-based systems. A major thrust will be to design new electrode architectures in which an electrochemically active species is attached to the surface of a porous current collector providing a strong connection from the active species to the substrate. Such an approach minimizes the need for conductive additives and increases the power capabilities of these high energy anodes.

**STATUS OCT. 1, 2011:** A series of new electrode structures will have been synthesized and evaluated that use elemental silicon and tin as the active material. The energy and power advantages of three-dimensional electrode architectures when compared to two dimensional anode structures will be quantified. Electrodes that utilize metallic copper as both the binder and conductive additive will have been evaluated. Methods to create the three dimensional copper current collector around the active materials, notably silicon, will have been developed.

**EXPECTED STATUS SEP. 30, 2012:** The interfacial structure of silicon-based electrodes bound to the substrate using metallic binders will have been determined. Studies will have been initiated on the deposition of silicon and tin into porous substrates and developed characterization tools to study active material / current collector interactions and their effect on cycle life and fade rate.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

#### **MILESTONES:**

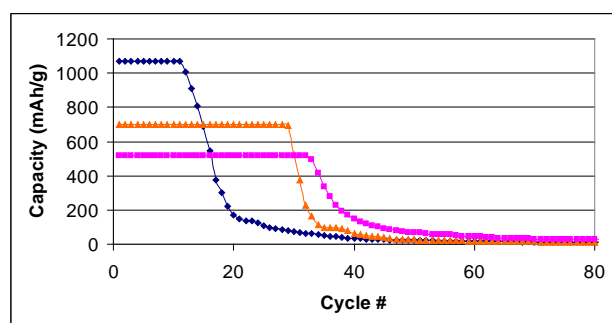
- (a) Complete characterization of the interfacial region in Cu-Si metallic electrodes. (Mar. 12) **Complete**
- (b) Characterize the phases formed and extent of electrode homogeneity for a series of electrodeposited Sn-based electrodes. (Sep. 12) **On schedule**
- (c) Assess the role of electrolytes and irreversible capacity and SEI formation in three-dimensional electrode structures. (Sep. 12) **On schedule**
- (d) Demonstrate the benefit of polymeric surface coatings on the cycle life of three-dimensional electrode structures. (Sep. 12) **On schedule**



## PROGRESS TOWARD MILESTONES

Team: Fulya Dogan, Lynn Trahey (Argonne National Laboratory)

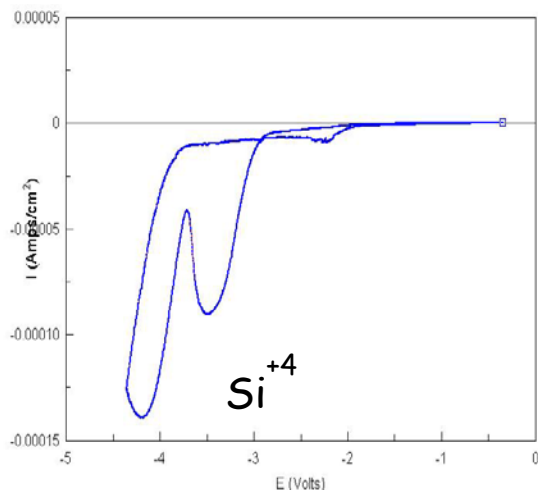
Working electrode structures are composed of many interdependent parts, notably active materials, binders, current collectors, and conductive additives. The dispersion and interactions between these components is critically important in determining cycle life, aging effects, and capacity fade. Presently used formulations have been optimized for graphite powder and to some extent extrapolated to alternative anodes, including Si, intermetallics, and metal oxides. Typical electrodes for these non-graphitic anodes fail earlier than graphite-based system due in part to the stresses the lithiation puts on the other electrode components. In trying to develop a more robust and functional electrode structure we have used the very large observed expansion of Si on lithiation as a test system for developing simpler and more functional Li-ion battery electrodes. Previous reports discussed our initial efforts in developing methods to encase micron-size Si particles with a Cu net formed using an *in situ* process and optimizing the annealing procedure to create a mesh over the micro-sized Si binding it to the current collector without the need for additional binders or conductive additives.



**Figure 1.** The cycling capacity of a series of  $\text{CuSi}_4$  electrodes cycles to  $\text{LiSi}$ ,  $\text{Li}_3\text{Si}_4$ , and  $\text{LiSi}_2$ .

Figure 1 highlights the effect of volume expansion on the stability of the Cu-metal binder-based electrode. A milestone for this year, to determine the role of the annealing and how best to describe the interface between the Cu and Si, has been completed. Powder

XRD was used to determine the various temperature limits and identify the phases that formed. Electrochemical cell testing was used to determine relative activity of the Si (Cu-Si alloys are inactive). Solid state NMR has been used to assess the phases that formed in samples that performed poorly but appeared to not alloy. In these NMR studies, the formation of a thin  $\text{Cu}_3\text{Si}$  layer between the Cu web and the active Si was correlated with poor cycling performance and the formation of an amorphous  $\text{SiO}_2$  in electrodes (from the processing) was also correlated to very poor performance. The best performing electrodes all showed very little to no  $\text{Cu}_3\text{Si}$  formation as well as no amorphous silica.



**Figure 2.** Electrodeposition of silicon from a  $\text{SiCl}_4$  containing electrolyte.

This Cu-Si three-dimensional electrode effort has been expanded by studying the deposition of Si (as  $\text{Si}^{4+}$  or  $[\text{Si}_4]^{4+}$ ) from solution onto Cu substrates of varying porosity and pore dimension. Figure 2 highlights some of the conditions used to deposit Si from  $\text{SiCl}_4$  at -3.5V (vs. Pt pseudo reference). Work to evaluate conditions that will form conformal coatings in porous structures will be continued.

**TASK 2.2 - PI, INSTITUTION:** Stanley Whittingham, Binghamton University

**TASK TITLE - PROJECT:** Anodes – Metal-based High Capacity Li-ion Anodes

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Cost, safety and volumetric capacity limitations of lithium-ion batteries

**OBJECTIVES:** To replace the presently used carbon anodes with safer materials that have double the volumetric energy density, and will be compatible with low cost layered oxide and phosphate cathodes and the associated electrolyte.

**GENERAL APPROACH:** Our anode approach is to synthesize, characterize and develop inexpensive materials that have a potential around 500 mV above that of pure lithium (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites at the nano-size. Tin will initially be emphasized, building on what was learnt from our studies of the tin-cobalt anode, the only commercial anode besides carbon. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal, kinetic and structural stability to gain an understanding of their behavior.

**STATUS OCT. 1, 2011:** It has been shown that bulk crystalline metals have a high capacity, react readily with lithium but that their capacity faded rapidly after several deep cycles in carbonate-based electrolytes; their behavior was no better under shallow cycling. In contrast, it has been shown that amorphous nano-size tin alloys, unlike pure tin, have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like cobalt. A nano-tin material that shows electrochemical behavior comparable to that of the Sn-Co alloy but without the need for cobalt was successfully formed by mechanochemical synthesis. It has also been shown that small amounts of silicon enhance the cyclability of aluminum.

**EXPECTED STATUS SEP. 30, 2012:** Our proposed work will result in the development of durable metal-based Li-ion battery anodes with volumetric energy densities that approach double those of the state-of-the art carbons. Nano-tin materials will have been synthesized by at least two different approaches and then characterized, to determine their morphology and electrochemical behavior. Clues as to how to control the SEI on such materials to optimize lifetime will have been gathered.

**RELEVANT USABC GOALS:** 5000 deep and 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit, and maximum system volume.

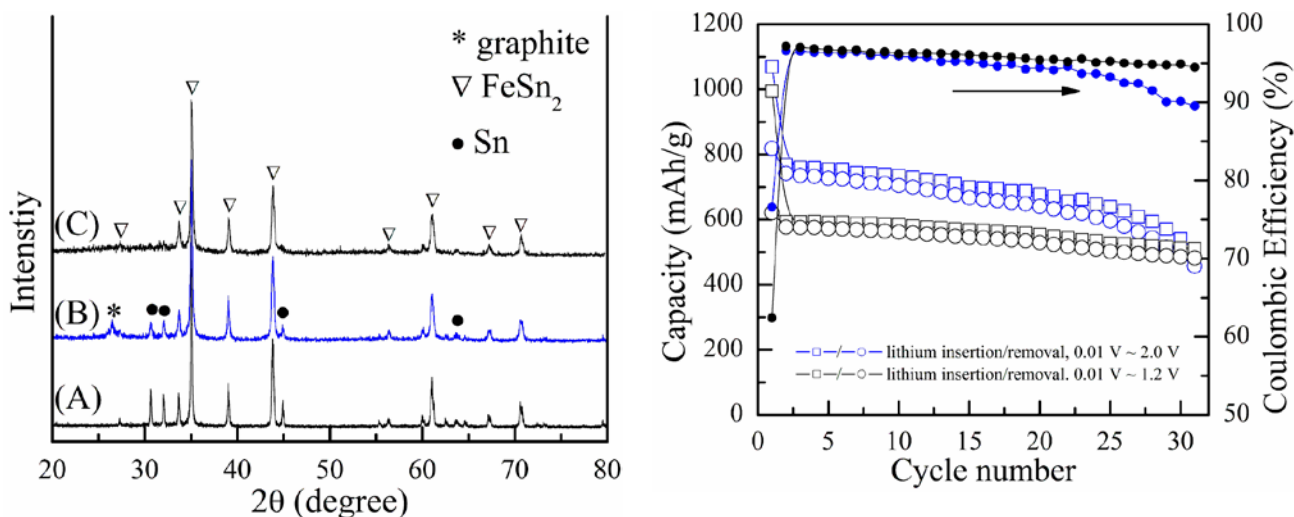
**MILESTONES:**

- (a) Synthesize a nano-size Sn material by a second method. (Dec. 11) **Complete**
- (b) Have the nano-size Sn meet the gravimetric capacity of the Sn-Co-C electrode and exceed the volumetric capacity of the Conoco Philips CPG-8 Graphite. (Mar. 12) **On schedule**
- (c) Determine the limitations to the electrochemical behavior of the mechanochemical Sn; characterize these materials and determine their electrochemical behavior. (Sep. 12) **On schedule**
- (d) Determine the electrochemistry of a new synthetic nano-Si material. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

The goal of this project is to synthesize new tin- and silicon-based anodes that have double the volumetric capacity of the present carbons, without diminishing the gravimetric capacity.

**Milestones (a) and (b) nano-tin anodes.** This quarter, the synthesis and characterization of a Sn anode by a second method, solvothermal, was completed. The  $\text{Sn}_2\text{Fe}$  composition was pursued because of its excellent capacity and capacity retention on cycling. In the solvothermal method,  $\text{FeCl}_3$  and  $\text{SnCl}_2$  were dissolved in ethanol and then transferred into a Teflon jar. Excess  $\text{NaBH}_4$  was poured into the solution before the start of the reaction followed by a solvothermal treatment, which was performed at  $200^\circ\text{C}$  for 24 hours. The XRD patterns in Fig. 1 show that the resulting powder contains  $\text{FeSn}_2$  with a small amount of Sn metal. Ball milling this compound with carbon removes the excess Sn metal. The  $\text{FeSn}_2$  particle size is less than 100 nm. The electrochemical cycling of the Sn-Fe-C compound is also shown in Fig. 1 (right) for two different voltage cycling regimes. The poor cycling efficiency may be improved to over 99% by ball milling with carbon; however this results in a drop in the capacity to between 400 and 500 mAh/g of total weight of the SnFe material + carbon.



**Figure 1.** (left) XRD patterns of (A) Solvothermally formed Fe-Sn; (B) Planetary ball-milled (pBM) Sn-Fe-C composite; (C) High-energy ball-milled (HEBM) Sn-Fe-C composite. Note there is some Sn metal phase in the solvothermally formed material, but it disappears after high-energy milling with graphite. (right) Electrochemical cycling of this Sn-Fe alloy for two different voltage windows. The current was  $0.3 \text{ mA/cm}^2$  in the 1<sup>st</sup> cycle and then changed to  $0.5 \text{ mA/cm}^2$  thereafter.

**Further plans to meet or exceed milestones:** None

**Reason for changes from original milestones:** See above

### Publications and Presentations:

1. Ruigang Zhang, Shailesh Upreti and M. Stanley Whittingham, "Tin-Iron Based Nano-Materials as Anodes for Li-Ion Batteries," *J. Electrochem. Soc.*, **158** (12), A1498-A1504 (2011).
2. A number of presentations were made at the Materials Research Society meeting in Boston, December, 2011.

**Task 2.3-PI, INSTITUTION:** Prashant N. Kumta, University of Pittsburgh

**TASK TITLE:** Anodes – Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low specific energy and energy density, poor cycle life and coulombic efficiency, large irreversible loss, poor rate capability, and calendar life.

**OBJECTIVES:** To identify new alternative nanostructured anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The objective is to replace carbon with an inexpensive nanostructured composite exhibiting higher capacity (1200 mAh/g) than carbon while exhibiting similar irreversible loss (<15%), coulombic efficiency (>99.9%), and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, cycle life, coulombic efficiency, and irreversible loss limitations of silicon based electrodes.

**GENERAL APPROACH:** Our approach is to search for inexpensive silicon, carbon, and other inactive matrix based composites (powders rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of Li, and 2) a capacity of 1200 mAh/g or greater (>2600 mAh/ml). Research will be focused on exploring novel economical methods to generate nanoscale heterostructures of various Si nanostructures and different forms of C derived from graphitic carbon, nanotubes (CNT) and new binders. Other electrochemically inactive matrices will also be explored. Promising electrodes will be tested in half cells against Li and compared to graphite as well as in full cells. Electrode structure, microstructure, rate capability, long and short term cyclability, coulombic efficiency, SEI origin and nature will also be studied.

**STATUS OCT. 1, 2011:** Nano-scale electrodes comprising Si-graphitic carbon-polymer derived C, and CNT related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C hetero-structures exhibit stable capacities of 700-3000 mAh/g.

**EXPECTED STATUS SEP. 30, 2012:** Efforts will continue to generate nano-composite ‘core-shell’, random, and aligned structures of varying nanoscale Si morphologies, boron (B), and C nanotubes exhibiting 1500 mAh/g and higher capacities. Research will be conducted to generate novel binders, study the synthesis conditions, nano-scale microstructure affecting the energy density, rate capability, first cycle irreversible loss and coulombic efficiency, characterize the SEI layer, and outline steps to yield stable capacity, reduce irreversible loss and increase coulombic efficiency.

**RELEVANT USABC GOALS:** Available energy for CD Mode, 10 kW Rate: 3.4 kWh (10 mile) and 11.6 kWh (40 mile); Available Energy for CS Mode: 0.5 kWh (10 mile) and 0.3 kWh (40 mile); 10s peak pulse discharge power: 45 kW (10 mile) and 38 kW (40 mile); Peak Regen Pulse Power (10 sec): 30 kW (10 mile) and 25 kW (40 mile); Cold cranking power at -30°C, 2sec-3 Pulses: 7kW; Calendar life: 15 years (at 40°C); CS HEV Cycle Life, 50 Wh Profile: 300,000 Cycles

**MILESTONES:**

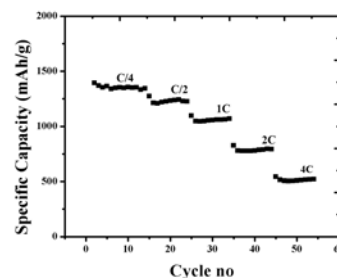
- (a) Achieve stable reversible capacity of 1500 mAh/g or higher (Mar. 12). **On schedule**
- (b) Achieve irreversible loss ( $\leq 15\%$ ) and efficiency ( $\geq 99.95\%$ ) to match carbon (Sep. 12). **On schedule**

## PROGRESS TOWARD MILESTONES

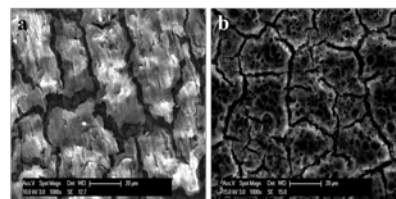
In the previous report (Q4-2011), the synthesis of thin amorphous Si films (*a*-Si) on Cu foil by electrodeposition from  $\text{SiCl}_4$ -based electrolytes was reported. These films showed a stable capacity of *ca.* 1300 mAh/g for over 100 cycles with very low capacity fade per cycle ( $<0.016\%$  per cycle for 100 cycles). In this quarter, the rate capability of the *a*-Si films, synthesized by electrodeposition, have been studied at different current rates varying from C/4 to 4C. Figure 1 shows the variation of the specific capacity with cycle number of an electrode discharged/charged at C/4, C/2, 1C, 2C, and 4C. The capacity retained at the discharge/charge rate of 1C is *ca.* 1000 mAh/g, which is *ca.* 77% of the capacity obtained at C/4 (*ca.* 1300Ah/g). This indicates that electrodeposited *a*-Si is a promising anode for Li-ion battery applications, including medium charge/discharge rates of *ca.* 1C. However, a significant capacity loss is observed when cycled at higher rates (2C and 4C), resulting in a capacity of *ca.* 520 mAh/g at 4C. This is due to the poor electronic or ionic conductivity of *a*-Si, rendering the charge transfer or Li alloying difficult. However, no capacity fade was observed for a given C rate and the resulting capacity at 4C is still much higher than the capacity obtained using pure graphite as an anode. Efforts are currently focused towards improving the conductivity of *a*-Si by exploring dopants to achieve better rate capability.

Figure 2 shows the morphologies of the as-synthesized film and the film after electrochemical cycling. The as-deposited film assumes a mud-crack morphology with islands of *a*-Si with size ranging from 10 to 20  $\mu\text{m}$ . In spite of 100 cycles of Li alloying and dealloying, there appeared to be no extension, modification, or growth of the crack widths or lengths in comparison to what was seen in the pristine film, consistent with long term stability (shown in Q4-2011). However, the film appears to have developed increased porosity upon cycling. Analyses of these pores that appear more like pits of varying depths are on-going. The origin of these pits is attributed to the possible erosion of impurities present in the form of salts in the electrolyte. Further studies are warranted to understand their nature and cause of formation.

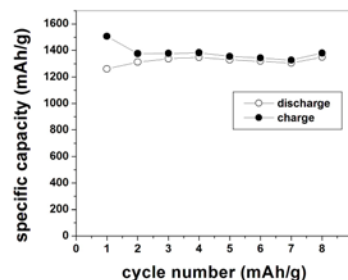
In order to achieve the targeted 15% first cycle irreversible capacity loss for Si/C, a composite based on Si nanoparticles and SFG graphite (*np*-Si/SFG) was synthesized by the low cost, viable, high-energy mechanical milling (HEMM) process. The variation of specific capacity with cycle number for the *np*-Si/SFG composite provided in Fig. 3 shows a 1<sup>st</sup> cycle discharge and charge capacity of *ca.* 1500 and *ca.* 1265 mAh/g, respectively, with an irreversible loss *ca.* 15%. A detailed surface morphological study will be performed on *np*-Si/SFG to understand the origin of the low irreversible loss that will, in turn, enable the design of the surface morphology for other high capacity, long cycle life anodes.



**Figure 1.** Specific capacity vs. cycle number of the *a*-Si film cycled at 0.25C, 0.5C, 1C, 2C and 4C.



**Figure 2.** SEM image of the *a*-Si film (a) after electrodeposition and (b) after 100 cycles.



**Figure 3.** Capacity vs. cycle number of *np*-Si/SFG composite.

**TASK 2.4: PRINCIPAL INVESTIGATOR, INSTITUTION:** Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

**TASK TITLE – PROJECT:** Anodes.-.Development of Silicon-based High Capacity Anodes

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy density, high cost, limited cycle life

**OBJECTIVES:** To develop high-capacity, low-cost electrodes with good cycle stability and rate capability to replace graphite in Li-ion batteries

**GENERAL APPROACH:** Our approach is to manipulate the nano-structure and conductivity of silicon (Si)-based anodes to improve their mechanical and electrical stability. Si-based nanostructures, including micro-sized Si particles with nano-pore structures and core-shell Si composite materials will be investigated. Interactions between Si-based anode and binders also will be investigated. PNNL's capabilities in *in situ* characterization (including *in situ* TEM and NMR) and modeling will be leveraged to investigate the fundamental fading mechanism in Si-based anodes.

**STATUS OCT. 1, 2011:** Porous silicon Si with micrometer particle sizes and different nano-pore sizes have been investigated for anode applications. The electrochemical performances of micro-sized Si particles with larger nano-pores have demonstrated improved performance. The porous Si powders have been coated with a thin layer (~6% in weight) of carbon by chemical vapor deposition (CVD) to increase their electrical conductivities. The porous structure of Si helps to accommodate the large volume variations that occur during Li-insertion/extraction processes. An initial capacity of ~1200 mAh/g (based on the full electrode) and capacity retention of ~800 mAh/g over 30 cycles were obtained at a 0.1C rate. In another effort, a SiC/SiO/C core-shell composite was developed. An initial capacity of ~1000 mAh/g (based on the full electrode) and capacity retention of ~600 mAh/g over 100 cycles were obtained.

**EXPECTED STATUS SEP. 30, 2012:** Micro-sized Si particles with large nano-pores will be prepared. An initial capacity of >1000 mAh/g (based on electrode) and capacity retention of ~700 mAh/g over 100 cycles will be obtained. A SiC/Si/C (or SiC/SiO/C) core-shell composite will be investigated further to improve its performance with a targeted initial capacity of >1200 mAh/g (based on the full electrode) and capacity retention of ~700 mAh/g over 100 cycles. The initial capacity loss of the electrodes will be minimized, and their coulomb efficiency during cycling will be increased further by selection of electrolytes and additives. The structure and evolution of the solid electrolyte interface (SEI) will be investigated by *in situ* microscopic analysis.

**RELEVANT USABC GOALS:** > 96 Wh/kg (plug-in hybrid electric vehicles [PHEV]), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

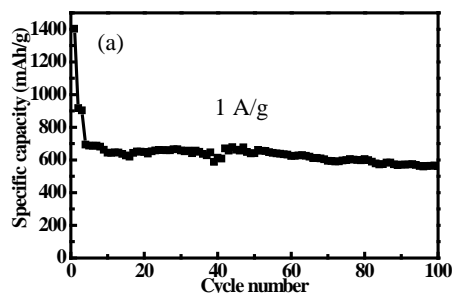
**MILESTONES:**

- (a) Identify the main failure mechanisms of the Si-based anode. (Mar. 12) **On schedule**
- (b) Improve the performance of Si based anode with a capacity-retention of >700 mAh/g over 150 cycles. (Sep. 12) **On schedule**
- (c) Select binders and electrolyte additive to improve the coulombic efficiency of Si-based anodes to more than 99%. (Sep. 12) **On schedule**

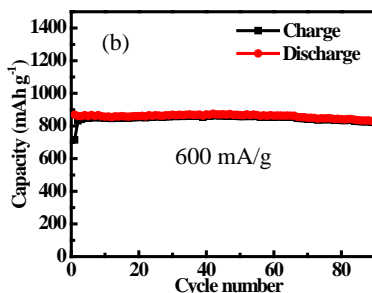
## PROGRESS TOWARD MILESTONES

Most milestones for FY11 have been met. A novel method was developed to synthesize Si nanoparticles from a commercial silicon product. A thin layer (*ca.* 5 nm) of CVD-coated carbon stabilized the electrical contact among Si particles and increased the electrical conductivity of the Si anode. Void space present between the Si and the carbon coating can absorb the volume change of Si on each charge. The porous Si anode retains 80% of its capacity after 100 cycles with a capacity of *ca.* 700 mAh/g (based on the entire weight of the electrode) at a current density of 1 A/g based on Si (equivalent to *ca.* C/3.7 for the Si).

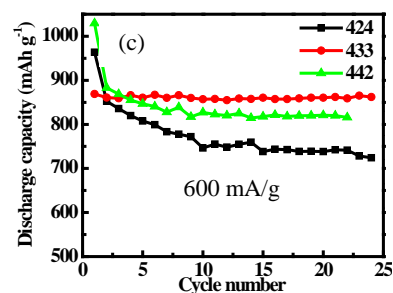
Further progress was made in Si anodes synthesized into a cycleable structure. A stable capacity of *ca.* 800 mAh/g (based on the entire weight of the electrode) over 90 cycles was obtained by anchoring the Si onto a conductive, rigid, structural skeleton and coating it with a conductive layer of graphene to promote continuous electrical contact (Fig. 1). Coin cell testing was performed between 0.05 and 1.5 V at a current density of *ca.* 250 mA/g (the first three formation cycles were tested at a current density of 100 mA/g). The ratio among Si, rigid skeleton, and conductive graphene coating greatly influences the cycleability. The best composition (Si: rigid skeleton: graphene) was found to be 4: 3: 3.



**Figure 1a.** Stable cycling of Si anodes with porous structure and continuous conductive carbon



**Figure 1b.** Stable cycling of Si anode with rigid skeletons.



**Figure 1c.** Cycling of Si anode with different Si, rigid skeleton, and conductive graphene composition.

The uniformity of the Si loading on the rigid structure frame requires further optimization. Electrolyte additives will be investigated to improve the cycling stability. Fundamental understanding of the structure of the SEI layer when electrolyte additives are introduced will be systematically investigated.

**Collaborations:** I.A. Aksay, Princeton University, and Vorbeck Inc. have provided the graphene for this work.

### Publication:

Chong-Min Wang, Wu Xu, Jun Liu, Ji-Guang Zhang, Lax V. Saraf, Bruce W. Arey, Daiwon Choi, Zhen-Guo Yang, Jie Xiao, Suntharampillai Thevuthasan, and Donald R. Baer, "In Situ Transmission Electron Microscopy Observation of Microstructure and Phase Evolution in a SnO<sub>2</sub> Nanowire during Lithium Intercalation," *Nano Lett.*, **11** (5), 1874–1880 (2011).



**TASK 2.5 - PI, INSTITUTION:** Anne Dillon, National Renewable Energy Laboratory

**TASK TITLE - PROJECT:** Anodes – Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIER:** Cost, low gravimetric and volumetric capacities, safety

**OBJECTIVES:** In this work, an inexpensive and scalable hot wire chemical vapor deposition (HWCVD) technique for the production of either amorphous silicon (a-Si) or nano-Si powders and/or doped a-Si or nano-Si will continue to be used. Novel atomic layer deposition (ALD) coatings that will enable durable cycling to be achieved for the high volume expansion Si materials (~ 400 %) will also be developed. Coatings and electrode design may also be demonstrated with commercially available crystalline nano-Si particles.

**GENERAL APPROACH:** The a-Si or nano-Si powders will be fabricated with HWCVD via silane decomposition on a hot filament. Growth parameters will be explored to optimize yield as well as incorporate dopants to produce more conductive a-Si as well as additives to improve cycling stability. Conventional electrodes containing active material, conductive additive and binder will be fabricated and subsequently coated via ALD that will serve as an artificial solid electrolyte interphase (SEI) and will importantly help minimize degradation upon volume expansion.

**STATUS OCT. 1, 2012:** This award was initiated at NREL in FY11. However, the University of Colorado was funded as of January 1, 2011. Collaborations with both Prof. M. Stanley Binghamton and Prof. Arumugam Manthiram, as well as with General Motors and LG Chem, are already in place. Samples will be sent to Prof. Clare Grey and she will perform *in-situ* NMR studies to provide mechanistic information about our ALD coatings.

**EXPECTED STATUS SEP. 30, 2012:** A thick Si anode with an ALD coating will be demonstrated to have a high durable capacity as well as high rate capability. Both gravimetric and volumetric capacities will be optimized.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

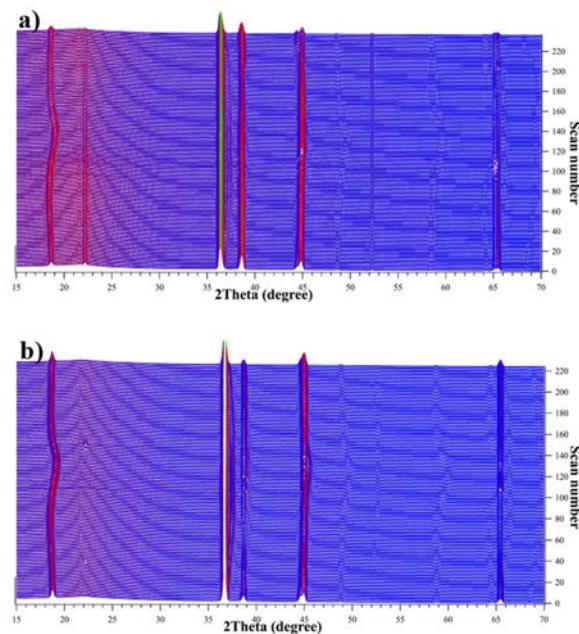
#### **MILESTONES**

- (a) Demonstrate mechanistic information about ALD coatings *via in situ* techniques including Raman spectroscopy, nuclear magnetic resonance and/or Time of Flight Secondary Ion Mass Spectrometry. (Jan. 12) **Complete**
- (b) Send an optimized thick electrode ( $\geq 15 \mu\text{m}$ ) with a reversible capacity of at least 2000 mAh/g at C/20 to Dr. Vince Battaglia at LBNL for verification. (May 12) **On schedule**
- (c) Demonstrate an ALD coating with rate performance of  $\geq \text{C}/5$  for a thick Si anode. (Jul. 12) **On schedule**
- (d) Demonstrate at least 50 cycles at a minimum of C/3 rate. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

(a) Show mechanistic information for ALD coatings via *in situ* technique. (Jan. 2012) **Complete**

In this report, the early completion of the January 2012 milestone to “demonstrate mechanistic information about ALD coatings with an *in situ* analytical technique” is discussed. To meet this milestone, the previously reported  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  cathode with 5 wt% carbon single-walled nanotubes (SWNTs) and 95 wt% active material (NMC) was produced. The binder-free electrode exhibited a capacity of *ca.*  $130 \text{ mAhg}^{-1}$  at 5C and nearly  $120 \text{ mAhg}^{-1}$  at 10C, for over 500 cycles at each current (collaboration with Whittingham at SUNY Binghamton). The electrode was cycled between 3 and 4.2 V *vs.*  $\text{Li/Li}^+$ . Using this electrode as a platform, it was coated with  $<1 \text{ nm}$  of  $\text{Al}_2\text{O}_3$  with the previously reported conformal ALD coating method. Both a bare-NMCSWNT and coated-NMCSWNT electrode were cycled between 2.5 and 4.5 V *vs.*  $\text{Li/Li}^+$ . Not surprisingly, a significant capacity fade, even at the moderate rate of C/2, for the bare-NMCSWNT electrode was observed, with capacity fading from *ca.* 190 to  $160 \text{ mAhg}^{-1}$  in 100 cycles. However, in the same voltage window, the capacity of the coated-NMCSWNT electrode remained fairly stable at 180 and  $130 \text{ mAhg}^{-1}$  at C/2 and 5C, respectively, with the rate alternating from moderate to high rate for 120 cycles. Thus, the ALD coating appears to have a significant stabilization effect on this electrode when cycling to higher voltage. Both electrodes were then cycled between 2.5 and 4.7 V *vs.*  $\text{Li/Li}^+$ , and *in situ* synchrotron XRD was performed during cycling at the Stanford Synchrotron Radiation Lightsource (SSRL). Figure 1 a) and b) display the *in situ* synchrotron XRD of the bare and coated-NMCSWNT electrodes, respectively. Approximately 230 X-ray scans were recorded over one complete charge/discharge cycle. The ripple in the line at low angle corresponds to the movement of Li-ions during a voltage hold at 4.7 V *vs.*  $\text{Li/Li}^+$ . In Fig. 1 a) for the bare-NMCSWNT electrode there is a distinct shift to lower angle for the peak at 45 degrees near the top of the plot (corresponding to the completion of a full cycle). This indicates that changes in the lattice parameters occur for the NMC material when cycled to a high voltage. In sharp contrast, no shift is observed for the same peak in Fig. 1 b) for the ALD coated-NMCSWNT electrode. This suggests that the thin ALD coating actually helps to preserve the structure of the NMC cathode when cycling to the high voltage. Electrochemical impedance spectroscopy measurements also indicated that the ALD coating helped to reduce charge transfer resistance and suppress interfacial reactions when cycling to high voltage.



**Figure 1.** *In situ* synchrotron X-ray diffraction of a) bare and b) coated-NMCSWNT electrodes cycled between 2.5-4.7 V.

**TASK 2.6 - PI, INSTITUTION:** Yury Gogotsi and Michel Barsoum, Drexel University

**TASK TITLE - PROJECT:** Anodes – New Layered Nanolaminates for Use in Lithium Battery Anodes

**BASLINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Needs increased life, capacity and improved safety.

**OBJECTIVES:** Replace graphite with a new material. Layered ternary carbides and nitrides known as MAX phases - may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, lesser expansion, longer cycle life and potentially, a lower cost than Si nanoparticles.

**GENERAL APPROACH:** Since at this time the relationship between capacity and MAX phase chemistry is unknown; a rapid screening of as many MAX phases as possible will be carried out to determine the most promising chemistry, by testing their performance in lithium ion batteries. This will be guided by *ab initio* calculations. Reducing particle size, selective etching of an A element out from the MAX structure, and exfoliation of these layered structure will also be investigated to increase the Li<sup>+</sup> uptake by these structures and improve the Faradaic efficiency.

**STATUS OCT. 1, 2011:** Based on the selection of the most promising MAX phases from the 60-phase family (guided by *ab initio* calculations) perform the testing of the binder-less material as Li-ion battery anodes. Reduce the particle size to < 1 μm and evaluate the effect of the particle size. Exfoliate MAX phases into nanolayers and conduct preliminary electrochemical studies using coin and swagelok-type cells.

**EXPECTED STATUS SEP. 30, 2012:** MAX-phase based anode formulation providing an optimum performance (capacity and cyclability) in a coin cell configuration.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

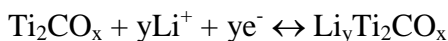
**MILESTONES:**

- (a) Reduce the particle size of MAX phase to submicrometer level and demonstrate a correlation between the particle size and the Li uptake capacity. (Mar. 12) **On schedule**
- (b) Partially/and or fully remove the A-group layer from the MAX phase (fully removing “A” layer resulted in exfoliation of MAX phases into graphene-like 2-D structure which were labeled "MXene") and study its effect on electrochemical behavior as anodes Li-ion batteries. (Sep. 12) **On schedule**
- (c) Produce anodes from MAX and/or MXene with the capacity of about 80% of the commercial graphite anodes. (Dec. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

HF treatment of  $\text{Ti}_2\text{AlC}$  (10% HF for 10h at RT) resulted in selective etching of Al and exfoliation of the  $\text{Ti}_2\text{C}$  layers.

Typical cyclic voltammetry curves at a rate of  $0.2 \text{ mV}\cdot\text{s}^{-1}$  for the exfoliated  $\text{Ti}_2\text{C}$  are shown in Fig. 1a. A broad, irreversible peak was observed around 0.6 V, during the first lithiation cycle (reduction); it was absent in subsequent cycles. It is reasonable to assign this irreversible peak to the formation of a SEI and its irreversible reaction with the electrode material. In all subsequent cycles, broad reversible peaks were observed at 1.6 and 2.0 V vs.  $\text{Li}^+/\text{Li}$  during lithiation and de-lithiation, respectively. Because these peak potentials are similar to those reported for  $\text{TiO}_2$  and lithiated titania, tentatively, these peaks are assigned to the following redox reaction:

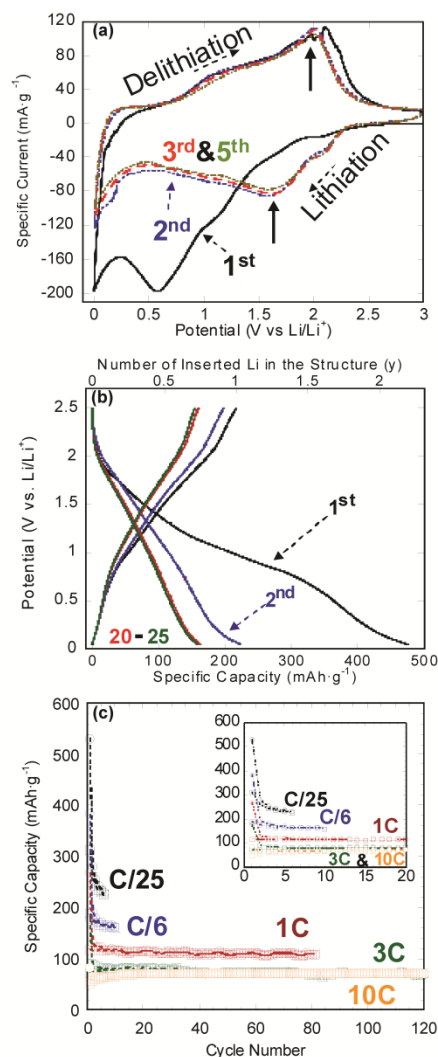


The rationale for this assignment is that drying at  $200^\circ\text{C}$ , prior to assembling the coin cells rids MXene of water or any OH species and leads to an oxygen terminated surface. As in the case of the titanates, even if the potentials vs. Li are relatively high, it is an advantage from a safety standpoint.

Figure 1b shows the galvanostatic charge/discharge curves at a rate of C/10 (1  $\text{Li}^+$  per formulae exchanged in 10 h). The capacity loss in the first cycle can again be attributed to a SEI layer formation at potentials below 0.9 V vs.  $\text{Li}^+/\text{Li}$ , as well as to the irreversible reduction of electrochemically active surface groups, such as fluorine or possibly hydroxyls.

At  $160 \text{ mAh}\cdot\text{g}^{-1}$ , the capacity of the treated powders is about 5 times higher than that of the as-received  $\text{Ti}_2\text{AlC}$  ( $\approx 30 \text{ mAh}\cdot\text{g}^{-1}$  at C/10) powders.

The specific capacities vs. cycle number at different cycling rates (C/25, C/6, 1C, 3C, and 10C) calculated from galvanostatic curves are shown in Fig. 1c. The highest capacity was obtained at a rate of C/25. The specific capacity values stabilize after 5 cycles, for all scan rates. At a C/25 rate, the capacity is  $225 \text{ mAh}\cdot\text{g}^{-1}$ , which corresponds to  $y \approx 1$ . At rates of 1 and 3 C, the capacities, after 80 cycles, were, respectively, 110 and  $80 \text{ mAh}\cdot\text{g}^{-1}$ . Even at rates of 10C, a stable capacity of  $70 \text{ mAh}\cdot\text{g}^{-1}$  was obtained for more than 200 cycles.



**Figure 1.** (a) Cyclic voltammetry curves of exfoliated  $\text{Ti}_2\text{C}$  at a constant scan rate of  $0.2 \text{ mV}\cdot\text{s}^{-1}$ . The solid arrows refer to main peaks positions during lithiation and delithiation cycles. (b) The galvanostatic charge/discharge curves at a C/10 rate. (c) Specific lithiation (circles in the figure) and delithiation (squares in the figure) capacities (per mass of active material) vs. cycle number at different rates. The inset in Fig. 2c is a zoom of the first 20 cycles [M. Naguib et al., *Electrochemistry Comm.*, 2012, doi:10.1016/j.elecom.2012.01.002]

**Task 2.7-PI, INSTITUTION:** Donghai Wang and Michael Hickner, Pennsylvania State University

**TASK TITLE - PROJECT:** Anodes – Synthesis and Characterization of Polymer-coated Layered SiO<sub>x</sub>-graphene Nanocomposite Anodes

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy, poor capacity cycling, large initial irreversible capacity.

**OBJECTIVES:** To seek mitigation of the electrochemical limitations of SiO<sub>x</sub> anodes during charge/discharge by designing novel SiO<sub>x</sub>-graphene nanocomposite and polymer binders to tolerate volume change, improve electrode kinetics, and decrease initial irreversible capacity loss. The new materials proposed and optimized fabrication strategies will improve the performance of SiO<sub>x</sub>-based anodes.

**GENERAL APPROACH:** Our approach is to synthesize SiO<sub>x</sub>-graphene nanocomposites to tolerate volume change upon lithiation/delithiation while maintaining Li-ion conductivity. Novel polymer binders will be developed with controlled elastic properties, ion-conductive moieties, and SiO<sub>x</sub> surface binding functionality, in order to stabilize and bridge SiO<sub>x</sub> particles. To improve the initial coulombic efficiency, SiO<sub>x</sub>-graphene nanocomposites to compensate for Li consumption upon irreversible conversion of SiO<sub>x</sub> into Li<sub>2</sub>O and Li silicates will be prelithiated.

**STATUS OCT. 1, 2011:** Si nanoparticles with controlled particle sizes and Si-graphene nanocomposites have been successfully synthesized via a solution approach. Several types of polymer binders with controlled SiO<sub>x</sub> binding groups and Li-conducting blocks have been synthesized. Processing parameters that control Si nanoparticle size and polymer functionality will be determined. Formation of SiO<sub>x</sub>/Si nanoparticles by coating SiO<sub>x</sub> layer onto Si nanoparticles and the corresponding SiO<sub>x</sub>-graphene nanocomposites will be also demonstrated.

**EXPECTED STATUS SEP. 30, 2012:** Evaluation of electrochemical performance of Si nanoparticles and Si-graphene nanocomposites will be completed. Processing parameters that control SiO<sub>x</sub> coating on Si nanoparticles and polymer functionality will be determined. The electrochemical properties of SiO<sub>x</sub>/Si nanoparticles and the novel polymer binders will be optimized, and their compositions and cycling protocols will be evaluated at LBNL BATT partner labs to confirm the initial results.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

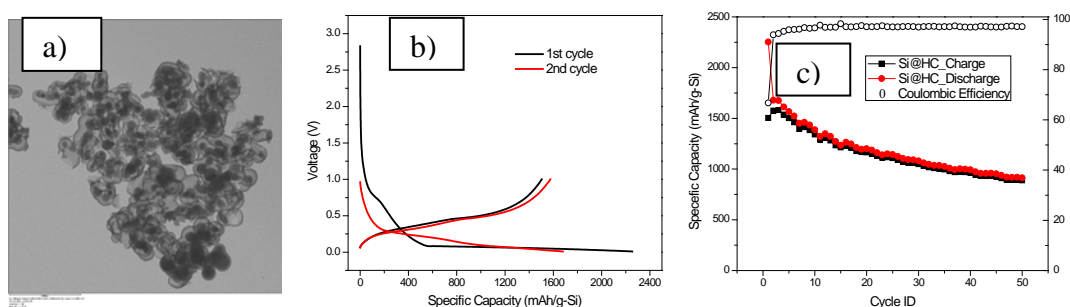
**MILESTONES:**

- (a) Demonstrate Si nanoparticles and Si-graphene nanocomposites that can achieve a reversible capacity of at least 1200 mAh/g and a cycle life of at least 50 cycles. (Dec. 11) **Complete**
- (b) Synthesize and characterize SiO<sub>x</sub>/Si nanoparticles, SiO<sub>x</sub>/Si-graphene nanocomposites, and binders with multiple functionalities. (May 12) **Complete**
- (c) Demonstrate SiO<sub>x</sub>/Si-graphene nanocomposite anode coated with novel binder with a reversible capacity of at least 1500 mAh/g within 100 cycles. (Sep. 12) **Complete**



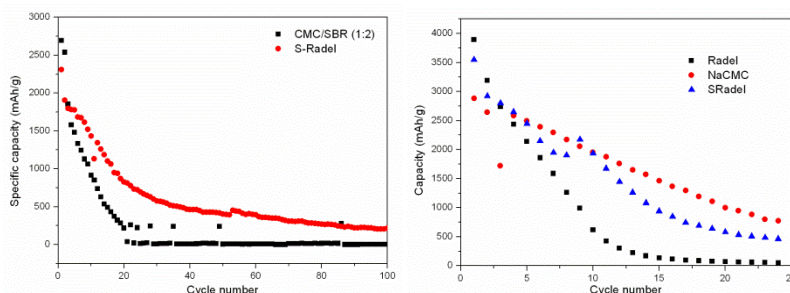
## PROGRESS TOWARD MILESTONES

**Si-based anode materials:** Conventional Si-carbon nanocomposites are composed of core-shell Si-carbon nanoparticles with intimate contact between Si and carbon. As the Si volume increases during discharge, the direct carbon coating may prevent volume expansion and lead to pulverization of the Si particles. An approach was developed to synthesize Si-hollow carbon (Si@HC) nanocomposites with commercial Si nanoparticles confined within hollow carbon spheres. Therefore, Si nanoparticles can expand/shrink freely during each discharge/charge process. The TEM images of the Si@HC (Fig. 1a) revealed that the Si nanoparticles were well encapsulated within the carbon spheres. The content of the Si in the nanocomposite is *ca.* 48 wt%. The optimization of the Si content and carbon hollow shell thickness are under investigation. It was found that the Si in the Si@HC exhibited a discharge capacity of around 2250 mAh/g Si for the first cycle at *ca.* 400 mA/g (equivalent to a C/5 rate) and a capacity of *ca.* 1000 mAh/g was obtained after 50 cycles. Compared with the fast capacity fade of commercial Si nanoparticles and conventional Si-carbon nanocomposites (data not shown), the cycle stability of the Si in the Si@HC is encouraging (Fig. 1c).



**Figure 1.** (a) Si@HC, scale bar: 1000 nm (b) discharge-charge profiles (c) capacity and coulombic efficiency vs. cycle number in 1M LiPF<sub>6</sub> EC-DMC-DEC (1:1:1).

**Polymer binders:** Extended cycling was performed on cells with different compositions of Radel-based polysulfone binders (Fig. 2). S-Radel showed significant improvements over CMC/SBR in initial cycles, but both types of binders cycled poorly beyond 20 cycles. The performance of Radel-based binders with different functionalities does not match the performance of Na-CMC. The composition for all cells shown here is Si:Super P:Binder 43:42:15. The initial cycling performance of mechanically stiff Radel polymers looked good, but the cycle life of these materials is not good enough at this point.



**Figure 2.** Comparison of polymer binders in cycling performance of Si-anode cells.

Optimizing the composition of the electrodes to learn more about the influence of polymer binder properties on the performance of Si anodes is continuing, and a move to higher polymer compositions that swell less in the electrolyte is seen. These continued tests on a range of polymer binders will give us insights into how new polymer binders may be employed to improve the performance of Si-based anodes. New crosslinkable polymer binders are currently being synthesized to try and combat the swelling of the binder in electrolyte and impart more robust mechanical properties to the electrode.

**TASK 2.8 - PI, INSTITUTION:** Yi Cui, Stanford University

**TASK TITLE - PROJECT:** Anodes – Wiring up Silicon Nanoparticles for High Performance Lithium-ion Battery Anodes

**BASELINE SYSTEMS:** Conoco Phillips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy density, low efficiency, short cycle life, and safety issues

**OBJECTIVES:** To overcome the charge capacity limitations of conventional carbon anodes by designing optimized nano-architected silicon electrodes 1) fabricate novel nanostructures that show improved cycle life, and 2) develop methods to study the lithiation/delithiation process to understand volume expansion for higher efficiency.

**GENERAL APPROACH:** This project explores new types of Si nanostructures to be used as lithium ion battery anodes. Specifically, a variety of hollow and porous nanostructures will be fabricated, and their performance will be compared with other nanostructures such as nanowires. These hollow/porous nanostructures could act to minimize external volume expansion and produce stable SEI layers that will lead to more efficient long-term cycling. In addition, separate efforts will be dedicated to understanding the fundamentals of volume expansion in Si nanostructures through single nanostructure observation. This project was initiated January 1, 2011.

**STATUS OCT. 1, 2011:** A variety of spherical, one-dimensional, tubular, and porous Si nanostructures will have been fabricated and incorporated into Si anode architectures. Critical size for fracture of various nanostructure geometries during lithiation/delithiation will be established.

**EXPECTED STATUS SEP. 30, 2012:** Anode cycle life, Coulombic efficiency, first cycle irreversible capacity loss, specific capacity, and mass loading will be optimized by varying synthesis conditions. Effect of hollow/porous structure on volume expansion and Coulombic efficiency will be identified. A detailed understanding of how volume expansion depends on nanostructure geometry will be advanced.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

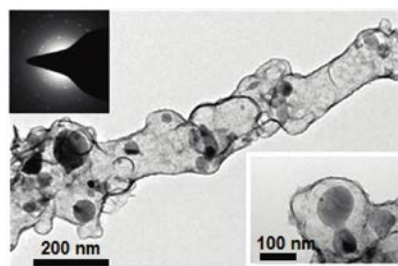
**MILESTONES:**

- (a) Fabricate hollow/porous nanostructured anode with high reversible capacity and high Coulombic efficiency. (Jan. 12). **Complete**
- (b) Determine effect of hollow structure on volume expansion, compare to non-hollow nanostructures. (Apr. 12) **On schedule**
- (c) Optimize nanostructure design for high mass loading and long cycle life (>1000 cycles). (Jul. 12) **On schedule**
- (d) Develop fundamental understanding of the features that control volume expansion/contraction in Si nanostructures (*i.e.*, Li diffusivity, Si mechanical properties). (Sep. 12) **On schedule**



## PROGRESS TOWARD MILESTONES

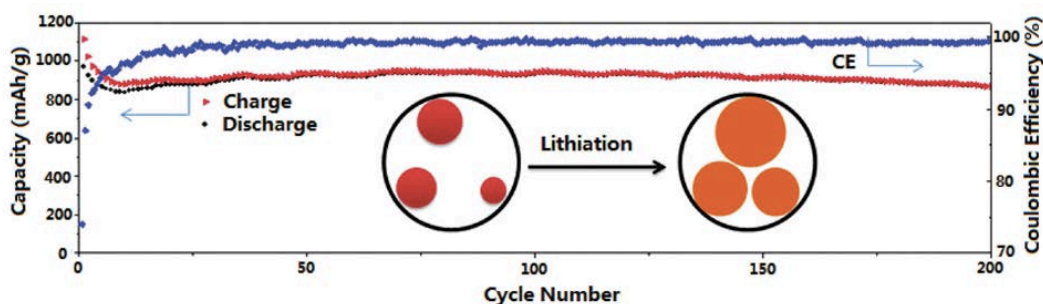
### Engineering Nanoparticle-Based Structures to Allow for Volume Expansion while Limiting SEI Formation.



**Figure 1.** TEM image of the hollow carbon/silicon nanoparticle structure1.

expansion/contraction and have exhibited improved electrochemical performance, issues related to low coulombic efficiency (CE) still persist in alloying anodes. This is in part because volume changes do not allow for a static surface on which a stable SEI can form; side reactions persist with cycling due to rupture of the SEI layer and continual exposure of Si material to the electrolyte. To combat this problem, a novel structure has been developed and tested in which Si nanoparticles are enclosed in a thin tubular carbon shell within which there is space for unimpeded volume expansion during lithiation, as shown in the TEM image in Fig 1. This design allows for the outer carbon layer to remain intact even after full

lithiation and expansion of the Si nanoparticles. Since the carbon layer is the only part of the structure exposed to the electrolyte, a mechanically stable SEI layer can form on the outer carbon shell. This composite material showed excellent cycling behavior in Li half-cells, retaining >85% of the initial discharge capacity after 200 cycles with CE >99% after the initial 50 cycles (Fig 2). This type of nanostructure design is expected to be useful in improving the performance of many different alloying anode materials.



**Figure 2.** Capacity with cycling for a hollow carbon shell/Si nanoparticle composite electrode. The inset is a schematic of the structure before and after lithiation.

***In situ* TEM of Silicon Nanowire Lithiation.** Studies have shown that metallic coatings can improve cycle life [Sethuraman, *J. Power Sources* 2011], but the effect of this type of coating on volume expansion is not well understood. *In situ* TEM has been employed using a specialized TEM/STM sample holder to study the effect of Cu coatings on volume expansion/contraction during lithiation/delithiation of Si nanowires. Coatings on one lateral nanowire surface remain intact after volume expansion and contraction, but the composite structures bend due to dimensional mismatch between the two layers during delithiation. In contrast, conformal Cu coatings fracture due to large hoop stresses that are generated during volume expansion. Notably, it was observed that Si has a tendency to expand away from Cu during lithiation, because Cu acts as a mechanical constraint and as an obstruction to Li diffusion. This new understanding can assist in the development of optimized structures that take both volume expansion and surface chemistry into account.

**TASK 2.9 - PI, INSTITUTION:** Kwai Chan and Michael Miller, Southwest Research Institute

**TASK TITLE - PROJECT:** Anodes – Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-ion Batteries

**BASELINE SYSTEMS:** Conoco Phillips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy density, low-power density, and short calendar and cycle lives

**OBJECTIVES:** The objectives are to synthesize and characterize silicon clathrate anodes designed to exhibit small volume expansion during lithiation, high specific energy density, while avoiding capacity fading and improving battery life and abuse tolerance.

**GENERAL APPROACH:** Our approach is to synthesize guest-free Type I silicon clathrate (Si<sub>46</sub>, space group  $Pm\bar{3}n$ ) using high-pressure and high-temperature experimental methods, including a newly-developed arc-melt technique. Concurrently, an investigational route for direct synthesis of guest-free clathrate will be explored, and *ab initio* and classical molecular dynamics (MD) computations to identify lithiation pathways will be performed. The silicon clathrates will be utilized to fabricate prototype silicon clathrate anodes. Electrochemical characterization will be performed to evaluate and improve, if necessary, anode performance including cyclic stability. The final year of the program will be directed at the design, assembly, and characterization of a complete (anode/cathode) small-scale, prototype battery suitable for concept demonstration.

**STATUS OCT. 1, 2011:** Batch quantities (1-2 grams) of Type I silicon clathrates will have been fabricated by down-selecting and adopting at least two synthetic approaches. Furthermore, computational results will have been obtained using first principles and classical theories to identify possible reaction pathways for the formation of clathrates, Li<sub>x</sub>Si<sub>46</sub>, and Li<sub>15</sub>Si<sub>4</sub>. Several half cells of clathrate anodes will have been fabricated.

**EXPECTED STATUS SEP. 30, 2012:** The most viable method of synthesizing Type I silicon clathrate will have been selected and optimized in terms of yield and purity. Scale-up of synthesis from small quantities (1-2 grams) to hundreds of grams via one or two methods will have been completed. Three different approaches to fabricating clathrate anodes on suitable substrates would have been explored and one selected for laboratory-scale measurements. The intrinsic electrochemical properties of these anodes will have been characterized using a half-cell test apparatus. Classical and *ab initio* computations will have continued with the aim of assessing the effects of metal alloying on Li<sup>+</sup> occupancy and lattice expansion, while identifying possible reaction pathways for intercalation and deintercalation of lithium.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

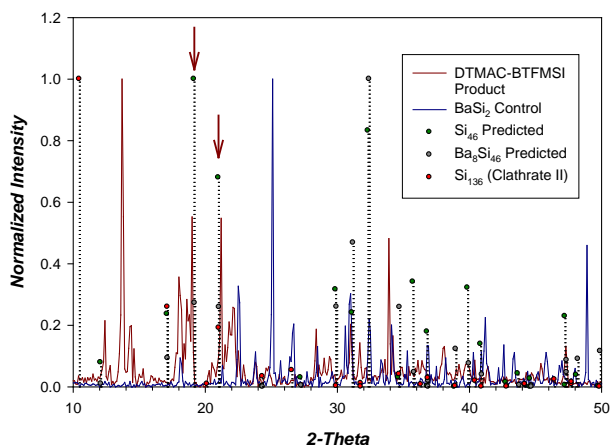
**MILESTONES:**

- (a) Select one synthetic pathway. (Dec. 11). **Complete**
- (b) Predict the Li<sup>+</sup> occupancy and lattice expansion potential of Type I metal-silicon clathrate alloys using classical and *ab initio* calculations. (Mar. 12) **On schedule**
- (c) Continue identifying possible reaction pathways for the formation of empty clathrates □Si<sub>46</sub>, Li<sub>x</sub>Si<sub>46</sub>, Li<sub>15</sub>Si<sub>4</sub>, and Li<sub>x</sub>M<sub>y</sub>Si<sub>46-y</sub>. (Jun. 12) **On schedule**
- (d) Synthesize hundreds of grams of Type I silicon clathrates and/or metal-silicon Type I clathrate alloys with complementary determination of structural purity. (Sep. 12) **On schedule.**

## PROGRESS TOWARD MILESTONES

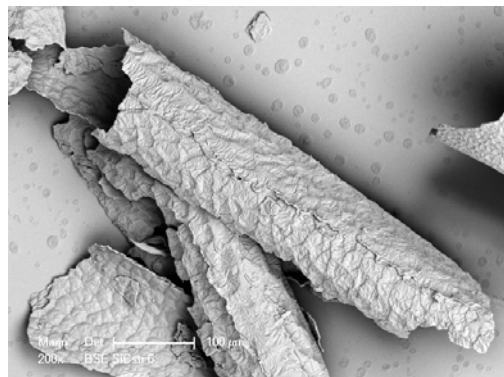
### Task 1 – Synthesis of Guest-Free Silicon Clathrate I

**Batch Synthesis via Soft Oxidation of  $\text{BaSi}_2$**  A systematic approach toward synthesizing and isolating guest-free Type I silicon clathrate ( $\text{Si}_{46}$ ) was undertaken this quarter using a solution-based, batch process (Hoffman-type elimination and soft oxidation reaction) under relatively mild conditions (*ca.* 300°C). Three different trial syntheses were carried out starting from a fine powder of  $\text{BaSi}_2$  dispersed in a series of ionic liquids (ILs) in which the hexafluorophosphate (HFP), bis(trifluoromethylsulfonyl)imide (BTFMSI), and aluminum tetrachloride (ATC) anions were employed. In this series, partial structural transformation of  $\text{BaSi}_2$  was observed in the powder XRD spectra only for the ATC system, but this reaction was accompanied by significant thermal degradation of the IL. To further improve the thermal stability of the reaction, a new IL consisting of the BTFMSI salt, which formed a liquid-phase eutectic near room temperature, was first synthesized and then incorporated into a fourth trial synthesis. The PXRD (Fig. 1) and Raman characterization of the isolated product showed nearly-complete transformation of the silicide to form  $\text{Si}_{46}$ . Efforts are currently underway to improve the purity of the reaction product by removing unreacted silicide and secondary phase byproducts (*i.e.*,  $\text{Si}_4$ ).



**Figure 1.** PXRD spectra of unpurified synthesis product compared with that of other compounds.

**Direct Synthesis via PEMS** A plasma-enhanced magnetron sputtering (PEMS) vacuum deposition chamber was employed in an attempt to synthesize  $\text{Si}_{46}$  particles by directing a silicon-argon plasma into a pool of IL. Two different ILs were utilized and both produced small quantities of  $\text{Si}_{46}$ , which was confirmed by Raman spectroscopy. Figure 2 presents an image of a  $\text{Si}_{46}$  particle synthesized by the PEMS technique.



**Figure 2.** SEM image of  $\text{Si}_{46}$  synthesized by PEMS.

### Task 2 – Molecular Modeling of Silicon Clathrates

The energy change associated with the formation of  $\text{Ba}_2\text{Li}_x\text{Al}_6\text{Si}_{40}$  was computed as a function of temperature and Li content to identify potential pathways and processing windows for inserting Li into the  $\text{Al}_6\text{Si}_{40}$  framework.

### Task 4 – Half-Cell Electrochemical Characterization

A three-electrode split-cell apparatus (1M  $\text{LiBF}_4$  1:1 ED:DMC, PP separator) was employed to characterize the electrochemical stability and charge/discharge capacity of previously-synthesized silicon clathrate anode materials -  $\text{Ba}_8\text{Al}_6\text{Si}_{40}$  and  $\text{Si}_{46}$ . Cycling measurements at slow rates (C/200) have thus far indicated that at least eight  $\text{Li}^+$  per unit cell can be intercalated into  $\text{Ba}_8\text{Al}_6\text{Si}_{40}$  while the majority of Ba guest atoms remain trapped in the clathrate framework. Thus,  $\text{Ba}^{2+}$  guest atoms in the framework are not readily removed or exchanged with  $\text{Li}^+$  electrochemically. Similar measurements on as-synthesized  $\text{Si}_{46}$  anode materials are on-going.

## **BATT TASK 3** **ELECTROLYTES**

**TASK 3.1 - PI, INSTITUTION:** Nitash Balsara, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Electrolytes – Development of Polymer Electrolytes for Advanced Lithium Batteries

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda high-energy layered (NMC)

**BARRIERS:** Needs improved cycle life, energy density and safety.

**OBJECTIVES:** Characterize PS-PEO electrolytes with LiTFSI against Li-metal anodes in symmetric cells, sulfur, and air cathodes. Use block copolymers to create mesoporous battery separators for conventional liquid electrolytes.

**GENERAL APPROACH:** Synthesize and characterize dry PS-PEO (and PS-PEO-PS) polymer electrolytes. Continue to characterize salt/polymer mixtures by AC impedance spectroscopy, and make DC measurements with Li|polymer electrolyte|Li cells to obtain Li transference numbers. Collaborate with members of the BATT Program to test stability of the electrolyte against electrodes (Li metal, sulfur, and air). Synthesize and characterize porous PS-PE polymer separators by synthesizing a block copolymer, blending with a homopolymer, and washing out the homopolymer to yield a porous block copolymer.

**STATUS OCT. 1, 2011:** Complete study of morphology on solubility of Li<sub>2</sub>S<sub>x</sub> in PS-PEO copolymers. Use membrane casting device to create Li|SEO| air cells. Identify ideal molecular weight of homopolymer for creating block copolymer-based separators. Cycle cells with an electronically and ionically conducting polymer binder in the cathode. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores.

**EXPECTED STATUS SEP. 30, 2012:** Complete study of effect of morphology on transference number in PS-PEO copolymers. Quantify dendrite resistance of SEO electrolytes in symmetric and full cells. Study polysulfide dissolution in Li|SEO/LiTFSI|S cells. Cycle Li|SEO|air cells. Optimize conductivity-morphology relationships in block copolymer-based separators with well-defined pores. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores. Build Li/SEO/FePO<sub>4</sub> cells with an electronically and ionically conducting polymer binder in the cathode with active loading greater than 50 wt%.

**RELEVANT USABC GOALS:** EV applications goals are a specific energy of 200 Wh/kg and a specific pulse power of 400 W/kg.

### **MILESTONES:**

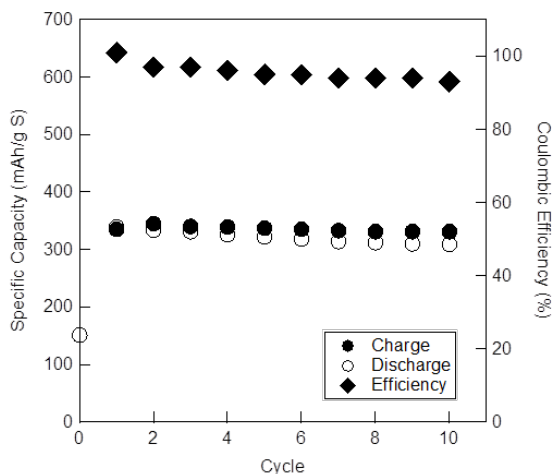
- (a) Complete transference number measurement as a function of morphology of SEO. (Dec. 11) **Complete**
- (b) Quantify improvement in dendrite resistance due to nanostructuring. (Mar. 12) **On schedule**
- (c) Report on improving cathode loading in Li/SEO/FePO<sub>4</sub> cells with electronically and ionically conducting binder. Target active material loading: 65 wt%. (Jun. 12) **On schedule**
- (d) Report cycling characteristics of Li/SEO/S and Li/SEO/air cells. (Sep. 12) **On schedule**
- (e) Report on conductivity and morphology of second generation porous block copolymer separators and demonstrate performance comparable to Celgard. Target conductivity: 0.4 mS/cm. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

Milestone 3.1a is complete. The measurements were performed on a variety of SEO block copolymers using both a rigorous electrochemical method and pulsed-field-gradient NMR. The  $\text{Li}^+$  transference number for SEO block copolymers was measured at  $0.6 \pm 0.1$ , which is similar to the value measured for PEO homopolymer.

For milestone 3.1b, batteries have been cycled to demonstrate the dendrite resistance of SEO block copolymer electrolytes. A number of ( $\text{LiFePO}_4$ -SEO-Li) batteries currently running have reached 400 cycles. The charge passed through these batteries is as much as 1 order of magnitude greater than that passed through equivalent symmetric (Li-SEO-Li) cells that have been studied. The effect of polymer molecular weight and electrolyte thickness is also being examined. In addition, we are designing experiments to image dendrites as they form in real time.

Milestone 3.1c is on schedule. Cells with cathodes containing 70 wt% active material are currently being cycled, with observed capacities approaching theoretical values.



**Figure 1.** Cycling data for Li|SEO|S cells.

Recent work toward milestone 3.1d has involved testing new types of catalyst to further reduce fade of the Li-SEO-air batteries. Wide angle X-ray scattering (WAXS) will be performed on the batteries and control samples in the coming week in order to determine the charge and discharge products. This should give us better insight into reactions, *i.e.*, if electrolyte degradation is contributing to the capacity fade. In addition, preliminary cycling of Li|SEO|S cells continues. Capacities greater than 300 mAh/g sulfur have been obtained at a rate of 40  $\mu\text{A}$  for 10 cycles and a sulfur loading of 40%. Additional testing and optimization is ongoing.

Work towards milestone 3.1 (e) is ongoing and on schedule. A new set of 3 SES block copolymers has been synthesized with polystyrene block molecular weight held constant, while varying the polyethylene molecular weight. The conductivity of these separators in electrolyte has been measured as a function of  $\alpha$  ( $\alpha = N_{\text{PS,Homo}}/N_{\text{PS,BCP}}$ ). The highest conductivity measured in each of these membranes was around 0.4 to 0.5 mS/cm. In addition, while  $\alpha$  had a strong effect on conductivity, the peak conductivity occurred at different values of  $\alpha$  for each polymer. SEM and X-ray experiments will be used to determine the differences in morphology of these membranes.

**TASK 3.2 - PI, INSTITUTION:** John Kerr, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Electrolytes – R&D for Advanced Lithium Batteries

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Poor cycle and calendar life, low power and energy densities, particularly at low temperatures (-30°C).

**OBJECTIVES:**

- Determine the role of electrolyte structure upon bulk transport and intrinsic electro-chemical kinetics and how it contributes to cell impedance (Energy/ power density).
- Determine chemical and electrochemical stability of electrolyte materials to allow elucidation of the structure of and the design of passivating layers (*e.g.*, SEI).

**APPROACH:** A physical organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the processes that may affect the performance of the battery. This involves model compounds as well as synthesis of new materials to test hypotheses which may explain battery behavior.

**STATUS OCT. 1, 2011:** Initial studies on composite electrodes using single-ion conductor binders will be complete with the focus area materials: High voltage Ni-Mn Spinel cathodes and Conoco Philips CPG-8 Graphite anodes. Experiments will be complete on the use of modified multiwalled carbon nanotubes and carbon blacks for preparation of improved composite electrodes. The TGA/GC/MS system will be used to identify SEI components. Work on high volume expanding anodes with single-ion conducting binders and modified conducting additives will be extended to Si-based alloys. Dry polymer systems will be tested with LiFePO<sub>4</sub> and non-lithium metal anodes.

**EXPECTED STATUS SEP. 30, 2012:** Carbon nanotubes and other carbonaceous conducting elements will be further modified with a broader range of chemical groups (PEGs, imide and malonato-difluoroborate anions) and the effects on composite electrode performance determined. Combination of these modifications with variations of binder polymers will be studied to determine how electrode ink formulation affects the electrode morphology and electrode performance particularly for thick, high energy electrodes.

**RELEVANT USABC GOALS:** *Available energy:* 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power:* 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life:* 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life:* 15 years (at 40°C); cold cranking capability to -30°C; abuse tolerance.

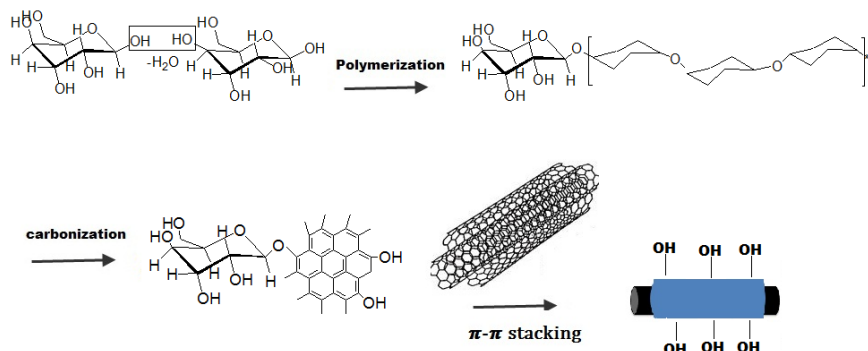
**MILESTONES:**

- (a) Determine the benefits of conducting element modifications on electrode performance. (Apr. 12). **On schedule**
- (b) Determine the role of electrode ink properties (*e.g.*, viscosity, stability, *etc.*) on electrode coating morphology and effects on electrode performance. (Sep. 12). **On schedule**

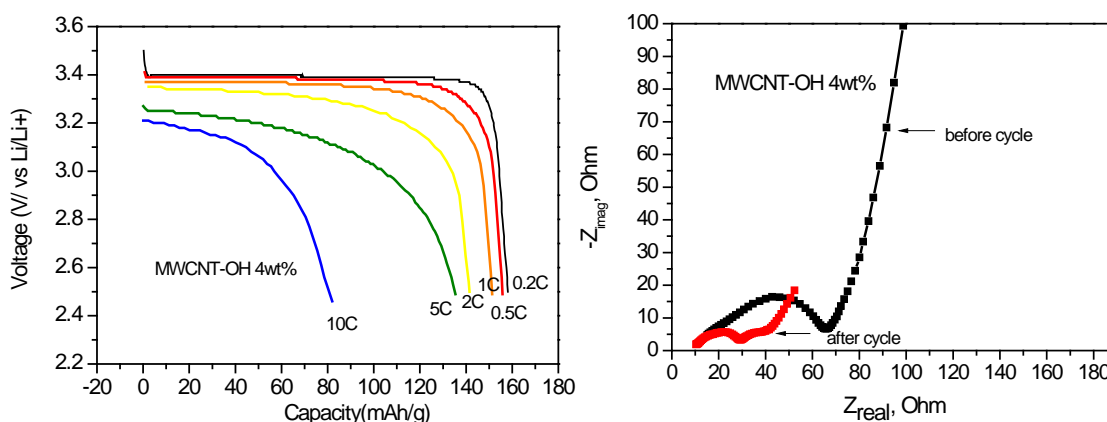


## PROGRESS TOWARD MILESTONES

Multiwalled carbon nanotubes (MWCNT) were modified with hydroxyl groups by a hydrothermal process using glucose as the precursor.



Glucose is polymerized on the MWCNT and then carbonized to leave a high concentration of hydroxyl groups on the surface of the MWCNT that can then be functionalized with anions such as triflate or fluoroalkylsulfonyl imides. The functionalized MWCNTs are then used as conducting additives for composite electrodes where the attached anions can influence the rates of the electrochemical reactions in the composite electrodes. The unfunctionalized MWCNTs show excellent performance themselves which appears to be due to the effect of the surface groups on the dispersion of the carbons in the electrode inks. The rate capability and impedance of Li half cells with  $LiFePO_4$  cathodes shows much better performance than the unmodified MWCNT electrodes and similar to those previously modified with sulfonated polystyrenes. This last observation indicates that the improvement in performance derives from better dispersion of the carbons in the electrodes.



**Figure 1.** Discharge performance of Li-LiFePO<sub>4</sub> cells (EC, EMC-LiPF<sub>6</sub> electrolyte) at RT (left) and EIS Nyquist plot before and after cycling (right).



**TASK 3.3 - PI, INSTITUTION:** Dmitry Bedrov, Feng Liu, University of Utah, and Oleg Borodin, Army Research Laboratory

**TASK TITLE - PROJECT:** Modeling – Molecular Modeling of Electrolytes and Electrolyte/Electrode Interfaces

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Poor low temperature operation, transport through SEI layer and cycle life. High interfacial resistance. Low energy and power density.

**OBJECTIVES:** Prediction of low energy surface structures and electrolyte reactivity for high voltage cathodes. Prediction and understanding of properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode. Improved understanding of electric double layer structure, capacitance and transport as a function of electrode potential and temperature for high voltage cathode. Prediction and investigation of structure and formation of the SEI at high voltage cathodes using reactive molecular dynamics (MD) simulations.

**GENERAL APPROACH:** Utilize DFT methodologies to investigate low energy surfaces of high voltage cathodes, investigate electrolyte reactions at cathode surfaces and investigate oxidative stability of electrolyte components. Develop reactive and non-reactive MD force fields and simulation methods to simulate high voltage novel electrolytes. Utilize reactive force field (ReaxFF) methods to study oxidation reactions and SEI formation at model cathodes with emphasis on additives and electrolyte oxidation at model cathodes.

**STATUS OCT. 1, 2011:** Investigation of electric double layer structure and charge transfer resistance as a function of electrode potential for model electrodes, investigation of conductivity of novel high voltage electrolytes, investigation study of SEI formation and role of additives for model anodes completed.

**EXPECTED STATUS SEP. 30, 2012:** Prediction of low energy surface structures and electrolyte reactivity for high voltage cathodes will be completed. Prediction and understanding of properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode will be completed for initial electrolytes and additives and compared with experiment. Prediction and investigation of structure and formation of the SEI at high voltage cathodes using reactive MD simulations will be completed for initial electrolyte compounds.

**RELEVANT USABC GOALS:** 10 s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile)

**MILESTONES:**

- (a) Predict low energy surface structures and electrolyte reactivity for high voltage cathodes. (Jan. 12) **On schedule**
- (b) Predict and understand properties of novel high voltage electrolytes and additives including oxidative stability and degradation products on the cathode. (Mar. 12) **On schedule**
- (c) Perform MD simulations of electric double-layer structure, capacitance and transport as a function of electrode potential and temperature for high voltage cathode. (Jun 12) **On schedule**
- (d) Predict and investigate structure and formation of the SEI at high-voltage cathodes using reactive MD simulations. (Sep 12) **On schedule**

## PROGRESS TOWARD MILESTONES

Oxidative stability of solvents. Previous calculations of the solvent/anion oxidative stability (Borodin, O; Jow, T.R, *ECS Transactions*, **33** (28) 77-84 (2011)) using the M05-2X/cc-pvTz functional were extended to additional solvent/anion pairs as shown in Table 1. Calculations were performed with the PCM model for three solvents with dielectric constants of 4.2, 20.5, and 78.4, and gas-phase

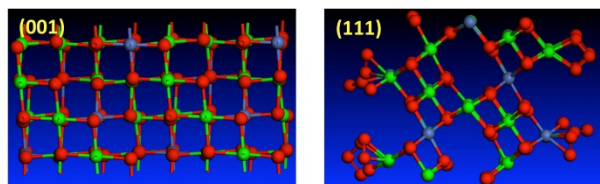
The spontaneous proton abstraction or HF formation was found for complexes where *both* solvent and anion had high intrinsic oxidative stability. However, in the solvent/anion complexes where one of the components had significantly lower oxidative stability than the other, no proton abstraction from the solvent was observed and anions with low oxidative stability such as difluoro(oxalate)borate (DFOB<sup>-</sup>) or dicyanotriazolate (DCTA<sup>-</sup>) oxidized. Similarly, in the VC/BF<sub>4</sub><sup>-</sup> complex, VC oxidized without any proton abstraction.

Table 1. Oxidative stability of the solvent/anion complexes.

complex	H or F transfer	ε=1	ε=4.2	ε=20.5	ε=78.4
DMC/BF <sub>4</sub> <sup>-</sup>	Yes	4.14	5.79	6.21	6.29
EC/BF <sub>4</sub> <sup>-</sup>	Yes	4.55	5.95	6.28	6.34
EC/LiBF <sub>4</sub> (v1)	Yes	8.74		6.64	
EC/LiBF <sub>4</sub> (v2)	Yes	8.46		6.82	
PC/BF <sub>4</sub> <sup>-</sup>	Yes	4.57		6.25	
FEC/BF <sub>4</sub> <sup>-</sup>	Yes	4.93	6.31	6.62	6.68
TMS/BF <sub>4</sub> <sup>-</sup>	Yes	5.23	6.33	6.49	6.52
EMS/BF <sub>4</sub> <sup>-</sup>	Yes	5.31	6.41	6.62	6.66
VC/BF <sub>4</sub> <sup>-</sup>	No	4.17	5.16	5.46	5.49
EC/ClO <sub>4</sub> <sup>-</sup>	YES	5.01		6.65	
EC/DFOB <sup>-</sup>	No			6.10	
EC/DFOB <sup>-</sup>	No			6.18	
EC/DCTA <sup>-</sup>	No	4.66		5.83	
EC/ClO <sub>4</sub> <sup>-</sup>	YES	5.01		6.65	

Surface energies of spinels. Using first-principles calculations, bulk and surface properties of both lithiated spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and delithiated spinel Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> were investigated. All of the spin-polarized calculations were carried out using density functional theory (DFT) and the GGA+U method that captured the localized nature of *d*-electrons of transition metal ions, which in turn allows for the accurate calculation of the transition-metal charge state. The calculated change in lattice constant from lithiated state LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> to delithiated state Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> in the bulk was found to be 1.3%, which is in good agreement with experimental measurement of 1.8%. The structural models of the stoichiometric (001), (110), and (111) surfaces of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> were constructed based on the obtained bulk crystal structures. For each surface, all possible planes for surface terminations were considered. Comparison of energies for stoichiometric surface cuts revealed that the (001) surface is the most stable surface, both for lithiated and delithiated spinels, in contradiction with experimental observations, where (111) surfaces dominate crystal formation.

However, investigation of delithiated, non-stoichiometric surfaces terminated with oxygens showed that the (111) surface is the most stable, with energy of the oxygen-terminated (111) surface lowest out of all surfaces (stoichiometric and non-stoichiometric) investigated. Therefore, our calculations indicate that the experimentally observed stability of the (111) surface is likely due to oxygen termination of this surface. The optimized structures of oxygen-terminated spinel surfaces are currently used for calculation of the electrolyte/surface interactions/reactions.



Ni <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub> surface energies (meV/Å <sup>2</sup> )				
Plane	(001)	(110)	(111)	
Configurations	1	1	1	2
Stoichiometric	62.67	74.47	74.87	82.90
Oxygen terminated	83.27	89.04	82.01	59.04

**TASK 3.4 - PI, INSTITUTION:** Khalil Amine and Larry Curtiss, Argonne National Laboratory

**TASK TITLE - PROJECT:** Electrolytes - Advanced Electrolyte and Electrolyte Additives

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Cycle/calendar life, abuse tolerance

**OBJECTIVES:** Develop advanced quantum chemical models to predict functional additives that form stable SEI on carbon anodes and cathodes and redox shuttles for overcharge protection. Synthesize suitable additives predicted by model, characterize and perform extensive cycle and calendar life tests.

**GENERAL APPROACH:** Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components using experiment and theory. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings for testing by experiment. Use density functional studies of graphite surface reactions to determine mechanisms for protective film formation from additives.

**STATUS OCT. 1, 2011:** Promising additive candidates obtained from our reduction potential screening will have been further investigated computationally for the initial decomposition step in formation of the SEI. Experimental testing and characterization of selected additives will be performed. Oxidation potentials for potential redox shuttles will have been calculated.

**EXPECTED STATUS SEP. 30, 2012:** Exploration of full decomposition pathways for selected additive candidates will be carried out using advanced quantum chemical techniques. Experimental testing and characterization of the additives will be performed. Quantum chemical studies of the reaction energies for decomposition of shuttle candidates and experimentally testing.

**RELEVANT USABC GOALS:** 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile)

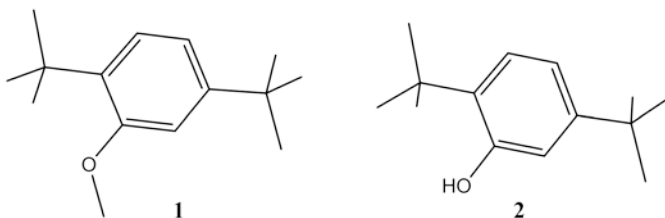
**MILESTONES:**

- (a) Use quantum chemical predictions of reaction energies for decomposition of redox shuttle candidates selected based on calculated oxidation potentials (Feb. 12) **On schedule**
- (b) Explore full decomposition pathways to formation of SEI for additive candidates based on salts, anhydrides, and carbonates will be carried out using advanced quantum chemical techniques. (Apr. 12) **On schedule**
- (c) Perform experimental testing of carbonate based additive candidates predicted from our computational model (May 12) **On schedule**
- (d) Perform experimental synthesis and testing of redox shuttles for overcharge protection. (Jul. 12). **On schedule**
- (e) Synthesize, characterize, and test selected carbonate-based additives from theoretical prediction. Identify at least one additive that significantly improves the cycle and calendar life. (Sep. 12). **On schedule**

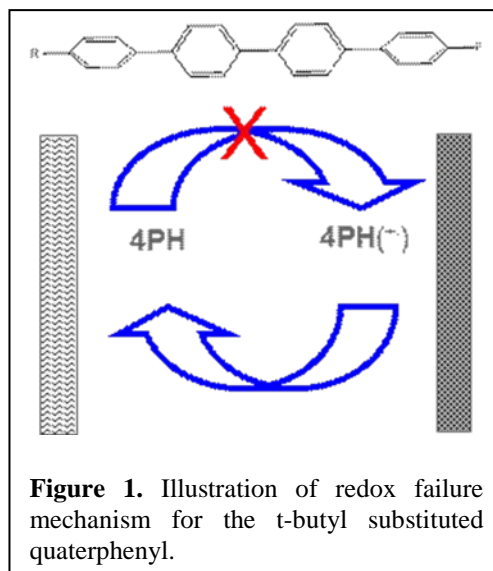
## PROGRESS TOWARD MILESTONES

Our approach for the development of new electrolyte additives for SEI formation involves screening of reduction potentials through use of accurate density functional methods followed by investigation of the mechanism of decomposition through investigation of reaction pathways. Finally the theoretical results are related to the performance of the additives in a battery cell. A good SEI prevents further electrolysis of the electrolyte and increases battery cycle life. Our database of additives has increased to over 365 species. All have been screened for reduction potentials and some further studied for decomposition pathways to form SEI components.

A new oligo(ethylene glycol)-functionalized compound, 2,5-di-*tert*-butyl-1,4-bis(2-methoxyethoxy)benzene (DBBB), has been found to be electrochemically reversible with very good overcharge protection properties. Density functional calculations provide an understanding of the increased solubility and overcharge stability properties of this new redox shuttle molecule. The calculated oxidation potential of the decomposition product 2,5-di-*tert*-butyl-1-methoxybenzene is 4.291 V compared to 3.819 V for the parent 2,5-di-*tert*-butyl-1,4-dimethoxybenzene. This is expected since methoxy groups release electrons to the benzene ring so removal of one methoxy group would make the molecule harder to oxidize. The calculated results compare favorably with the two oxidation peaks observed experimentally at 3.9 and 4.2 V. The decomposition reaction of 2,5-di-*tert*-butyl-1,4-dimethoxybenzene cation radical to form 2,5-di-*tert*-butyl-1-methoxybenzene cation radical plus formaldehyde is exergonic by 0.12 eV. A redox shuttle which has broken free of the polymer with one H arm and one OH arm has an oxidation potential of 4.272 V, which also agrees with the experimental results. Other decomposition pathways have been investigated also with similar conclusions.



Previously density functional calculations of a series of substituted quaterphenyls as potential redox shuttle candidate molecules were carried out and found to have oxidation potentials in the required range. The 4,4''-di-*tert*-butyl-*p*-quaterphenyl (4PH) compound has been synthesized, but it has a low solubility in the GEN2 carbonate electrolyte. Therefore, it was tested by coating the cathode with the 4PH compound dissolved in  $\text{CHCl}_3$ , followed by overcharging of the cathode. The cell only lasts for one cycle because the oxidation reaction of the redox shuttle (RS) at the cathode,  $\text{RS} \rightarrow \text{RS}^+$ , is followed by precipitation of RS on the anode from the  $\text{RS}^+ \rightarrow \text{RS}$  reaction on the anode. The reasons for this precipitation occurring on the anode are unclear, but must be prevented for this class of compound to be used as redox shuttles.



**Figure 1.** Illustration of redox failure mechanism for the *t*-butyl substituted quaterphenyl.

**TASK 3.5 - PI, INSTITUTION:** Brett Lucht, University of Rhode Island

**TASK TITLE - PROJECT:** Electrolytes - Development of Electrolytes for Lithium-ion Batteries

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Cell performance, life, cost: Calendar life: 40°C, 15 yrs; Survival Temp Range: -46 to +66°C; Unassisted Operating & Charging Temperature Range, -30 to + 52°C.

**OBJECTIVES:** Develop novel electrolytes with superior performance to SOA (LiPF<sub>6</sub> in carbonates). Develop and understanding of the source of performance fade in LiNi<sub>1.5</sub>Mn<sub>0.5</sub>O<sub>4</sub> cathodes cycled to high voltage (4.9 V vs. Li). Develop an electrolyte formulation that allows for superior performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathodes.

**APPROACH:** Optimize properties of LiPF<sub>4</sub>C<sub>2</sub>O<sub>4</sub>/carbonate electrolytes in small Li-ion cells at low temperature (-30°C) after accelerated aging. Investigate electrode surface films for cells cycled with LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>) to determine source of performance differences. Investigate cathode film forming additives for high voltage (> 4.5 V) cathode materials. Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation.

**STATUS OCT. 1, 2011:** Additional cathode film forming additives will have been developed for high voltage cathodes. An understanding of the source poor first efficiency for LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>) electrolytes on graphite anodes will have been developed. The low temperature performance of LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)/PC electrolytes after accelerated aging will have been investigated. Novel electrolytes to improve performance of Si-based alloy anodes will have been investigated.

**EXPECTED STATUS SEP. 30, 2012:** An LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>) electrolyte with optimized performance at low temperature after accelerated aging will have been developed. A better understanding of the role of electrolytes in the poor cycling efficiency and capacity fade of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathodes will have been developed. Novel electrolyte formulations which optimize the performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathodes cycled to high voltage (4.9 V vs. Li) will have been designed.

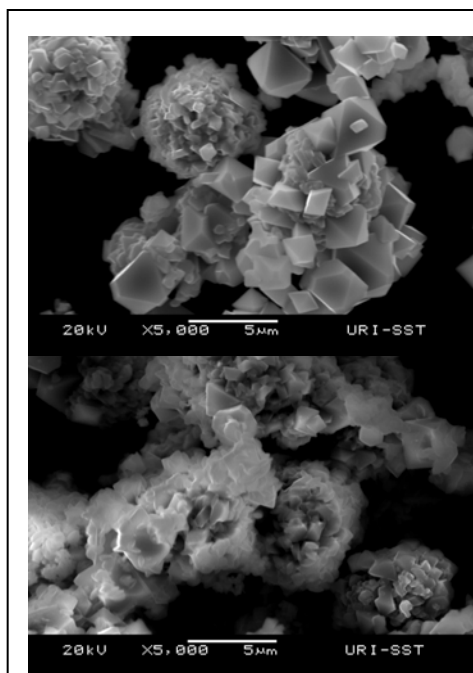
**RELEVANT USABC GOALS:** Calendar life: 40°C, 15 yrs; Survival Temp Range: -46–52°C; Cold cranking power at -30°C; Cycle life; Peak Pulse Discharge Power, 10 sec.

**MILESTONES:**

- (a) Develop an understanding of the role of electrolytes in capacity fade and poor cycling efficiency of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathodes. (Mar. 12) **On schedule**
- (b) Design electrolyte formulations to improve performance of high voltage Ni-Mn spinel cathode materials. (Jul. 12) **On schedule**
- (c) Optimize a LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>) electrolyte for graphite/LiNi<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>O<sub>2</sub> cells for high and low temperature performance. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

With regards to milestone (a): A detailed analysis was conducted of the role of electrolytes in capacity fade and poor cycling efficiency of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathodes cycled to high voltage. Also analyzed was the reaction of electrolyte with the surface of uncycled  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particles upon storage of the particles in SOA electrolyte at elevated temperature to simulate accelerated aging. After storage, the particles were analyzed *via* SEM (Fig. 1), XPS, and IR to monitor changes to the solid materials; and the liquid electrolytes will be analyzed *via* ICP-MS to detect Mn or Ni. The SEM images clearly indicate that the electrolyte significantly damages the cathode particles. Analysis of the surface of the cathode particles with XPS suggests a high concentration of electrolyte decomposition products on the cathode surface. Analysis of the electrolyte by ICP-MS indicates that 0.9% of the Mn and 0.3% of the Ni were dissolved into the electrolyte. Similar results were observed for storage at 55°C for two weeks. Our investigations into the mechanism of performance fade in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathodes cycled to high voltage has led to an understanding of two primary sources of performance fade. First, decomposition of the  $\text{LiPF}_6$  salt leads to the generation of Lewis acidic species that corrode the cathode surface and dissolve transition metals (Mn and Ni). Second, the high oxidation potentials of the cathode result in the oxidation of carbonate solvents to generate polyethylene carbonate, as previously reported. A better understanding of which of these problems contributes more to the performance fade of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathodes is being sought. Additives to address both of these problems are being developed, as discussed below.



**Figure 1.**  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  before storage in the SOA electrolyte (top) and after storage in SOA electrolyte for 2 weeks at 55°C.

With regards to milestone (b): Electrolyte formulations are being designed to optimize the performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathodes cycled to 4.9 V (vs. Li). Two primary types of additives are being investigated, the first of which is Lewis basic species which inhibits the thermal decomposition of  $\text{LiPF}_6$ . Preliminary investigations suggest that incorporation of Lewis basic additives inhibits Mn dissolution and improves cycling performance at high voltage. The second type of additive under investigation is cathode film forming. Cathode film forming additives are preferentially oxidized on the cathode surface to generate a passivation layer which inhibits electrolyte oxidation. After the study of several cathode film forming additives, improved cycling performance upon incorporation of the additives has been observed. Further details of our progress will be provided in future reports.

With regards to milestone (c): lithium tetrafluorooxalatophosphate ( $\text{LiPF}_4(\text{C}_2\text{O}_4)$ ) electrolyte formulations for good low temperature performance is under study. The investigations focus on the incorporation of methyl butyrate (MB) as a co-solvent and are in progress.

**Collaborations:** D. Abraham (ANL), M. Smart (NASA-JPL), V. Battaglia (LBNL), O. Borodin (ARL), W. Li (S. China Univ. Tech.), A. Garsuch (BASF), and Spinel Focus Group.

**TASK 3.6 - PI, INSTITUTION:** Daniel Scherson and John Protasiewicz, Case Western Reserve University

**TASK TITLE - PROJECT:** Electrolytes - Bifunctional Electrolytes for Lithium-ion Batteries

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Abuse tolerance

**OBJECTIVES:** Design, synthesize, and characterize physical, electrochemical, and interfacial characteristics of functionalized Li-salt anions containing phosphorus moieties known to impart materials with flame retardant properties (Flame Retardant Ions or FRIONs) and additional functional redox active groups capable of providing overcharge protection. Develop and implement ATR-FTIR spectroscopic methods for monitoring *in situ* the nature of products generated at Li-ion battery anodes under highly controlled conditions.

**GENERAL APPROACH:** Develop methods for the chemical functionalization of anions known to improve the performance of Li-ion batteries with covalently linked groups displaying flame retardant and/or overcharge protection attributes. Establish guidelines for the rational design and synthesis of optimized FRIONs and FROPs based on the analysis of results of testing in actual Li-ion batteries. Develop new *in situ* tactics for the application of attenuated total reflection Fourier transform infrared ATR-FTIR for the characterization of solution products generated at Li-ion battery anodes and solid electrolyte interfaces formed therein.

**STATUS OCT. 1, 2011:** Synthesis and purification of three cyclic triol borate (CTB) and one bicyclic borate phosphine oxide (CBPO) salts and determination of their flammability. Develop methods for the preparation of 100g of CTB-type compound for testing in actual batteries. Collect data using the *in situ* IRAS-FTIR cell for monitoring *in situ* the composition of the electrolyte and surface films on ultrapure Li metal in selected alkyl carbonate-salt formulations.

**EXPECTED STATUS SEP. 30, 2012:** Complete synthesis and characterization of three additional CTB-type and CBPO-type materials including flammability and electrochemical testing. Establish structure-electrochemical performance relationships within the CTB and CBPO anion families. Explore monocyclic FRION frameworks. Explore other synthetic routes towards Li-BOBPHO-R (R = Ph), especially those involving larger scale methods. Systematic *in situ* ATR-FTIR spectroscopic studies involving selected solvent formulations incorporating Case FRIONs both as main salts and additives.

**ELEVANT USABC GOALS:** No fire or rapid disassembly of cells during abuse conditions.

**MILESTONES:**

- (a) Prepare and fully characterize the electrochemical and flammability properties characteristics of three CTB-type compounds and one CBPO-type compound. (Oct. 11) **Delayed –due Jul. 12**
- (b) Expand the CTB-type and CBPO-type libraries of compounds. (Mar. 12) **On schedule**
- (c) Synthesize and characterize a monocyclic FRION. (Sep. 12) **On schedule**
- (d) Complete design, construction and testing of cell for *in situ* new infrared reflection absorption (IRAS) spectroscopy and impedance measurements with first (Oct. 11) **(delayed to Jul. 12)** and two additional Case electrolytes. (Sep. 12) **On schedule**
- (e) Perform full testing of three Case salts as full fledge electrolytes and as additives in actual batteries at Novolyte (Oct 11), and LBNL and ANL. (Sep 12) **On schedule**
- (f) Improve cycling by at least 15% to reach the same decay/end of life *vs.* the control electrolyte. (Sep 12) **On schedule**

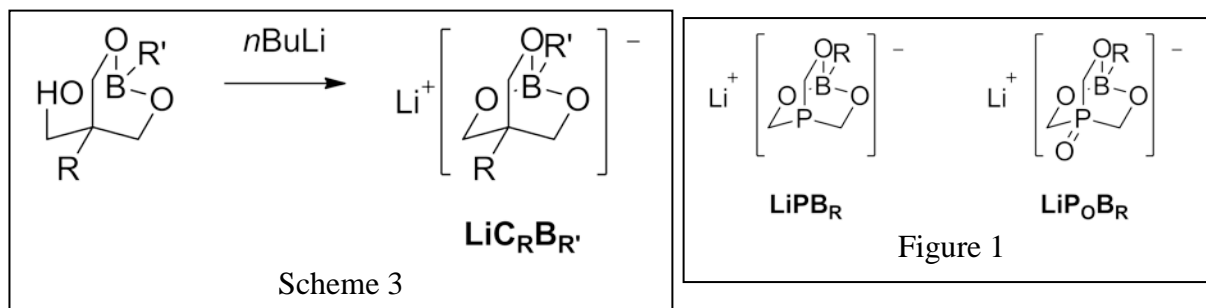


## PROGRESS TOWARD MILESTONES

**a. Synthesis and characterization of FRIONS** – Preliminary NMR spectroscopic data suggests that two new lithium cyclic triol borate salts ( $R = \text{Me}$ ;  $R' = n\text{Bu}$ , and 4-MeOPh) have been synthesized (Scheme 1 and Scheme 2, respectively; not shown). The lithium salt  $\text{LiC}_{\text{Me}}\text{B}_{n\text{Bu}}$  was prepared by a new route (Scheme 1), which is particularly promising as it avoids the synthesis and isolation of boronic acids.

The Li salt reported in a previous report,  $\text{LiC}_{\text{Me}}\text{B}_{\text{Cy}}$ , has been prepared in gram scale quantity.

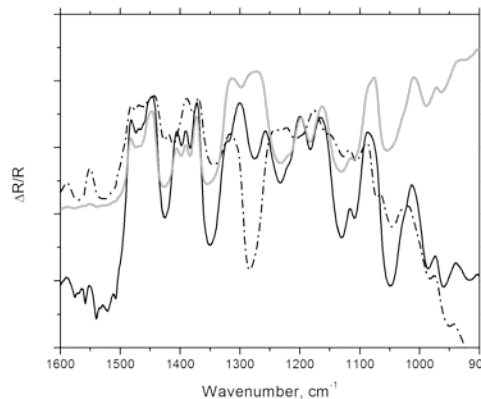
An alternate Li source,  $n\text{BuLi}$  (Scheme 3), as well as solvent free high temperature reactions were also investigated for the synthesis of cyclic triol borate salts but the results were comparable to those obtained with the previous method.



The FRION reported in a previous report,  $\text{LiP}_\text{O}\text{B}_{\text{OH}}$ , has been synthesized in quantities for full characterization and additional testing.

Efforts are ongoing for the synthesis of two new categories of FRIONS with a bicyclic structure analogous to cyclic triol borates which contain either a P(III) ( $\text{LiP}_\text{B}_\text{R}$ ) or the oxidized P(V) ( $\text{LiP}_\text{O}\text{B}_\text{R}$ ) at the bridgehead position (Fig. 1).

**b. In situ FTIR Measurements** – A large number of experiments were performed in the external reflection mode using a  $\text{CaF}_2$  window and p-polarized light to enhance surface spectral contributions. Data were collected in 1M  $\text{LiPF}_6$  in EC/EMC (3:7 by vol) with the Ni electrode pressed against the window and are displayed as customary as  $\Delta R/R = (R_{\text{ref}} - R_{\text{samp}})/R_{\text{ref}}$  vs wavenumber. Shown in Fig. 2, solid lines are the spectra of the solvent mixture without (grey line) and with the salt (black line) where  $R_{\text{ref}}$  is the empty cell. The spectrum in dotted lines was obtained by first depositing Li onto the Ni surface in the hanging meniscus configuration to form a passive film, and then pressing the electrode against the window during spectral acquisition. Interesting new features were observed in the latter spectrum in the region 1200 to 1350  $\text{cm}^{-1}$  not observed in the solution attributed to the passive film. These data are now being analyzed to determine the species responsible for these peaks.



**Figure 2.** *In situ*  $\Delta R/R$  vs. wavenumber for various sampling potentials, *samp*, as specified. See text for details.

**TASK 3.7 - PI, INSTITUTION:** Wesley Henderson, North Carolina State University

**TASK TITLE - PROJECT:** Electrolytes - Inexpensive, Nonfluorinated (or Partially Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low cost cell materials, abuse tolerance, low temperature performance

**OBJECTIVES:** Develop new anions as replacements for PF<sub>6</sub><sup>-</sup> or as additives for electrolytes

**GENERAL APPROACH:** Synthesize and fully characterize two classes of nonfluorinated (or partially fluorinated) anions: 1) chelated and non-chelated organoborate anions (related to bis(oxalate)borate (BOB<sup>-</sup>)), and 2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both Li salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as LiPF<sub>6</sub> and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion.

**STATUS OCT. 1, 2011:** Several synthesis procedures for new lithium salts have been developed. The characterization of the salts is in progress. Ionic liquids (ILs) have been prepared with *N*-alkyl-*N*-methylpyrrolidinium cations and the difluoro(oxalato)borate (DFOB<sup>-</sup>) anion. These ILs have been characterized as additives to electrolyte formulations.

**EXPECTED STATUS SEP. 30, 2012:** Extensive characterization of solvent-LiFSI and -LiDFOB mixtures will be completed. Several new lithium salts will be reported along with a comparison of their properties with conventional salts such as LiBF<sub>4</sub> and LiPF<sub>6</sub>. ILs will have been prepared from these anions and tested in IL-LiX and IL-LiX-solvent mixtures, as well as for use as additives to conventional electrolyte formulations.

**RELEVANT USABC GOALS:** Available energy: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); cycle life: 5000 cycles (10 mile) and 3000 cycles (40 mile); calendar life: 15 years (at 35°C); cold cranking capability to -30°C; abuse tolerance.

**MILESTONES:**

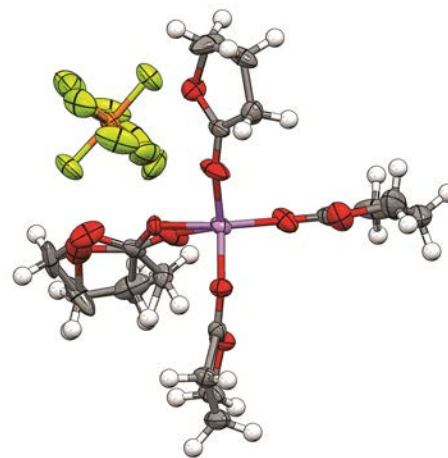
- Determine the phase behavior/properties of solvent-LiPF<sub>6</sub> mixtures. (Apr. 12) **On schedule**
- Determine the phase behavior/properties of solvent-LiFSI and -DFOB mixtures. (Sep. 12) **On schedule**
- Prepare/characterize lithium salts with partially fluorinated cyanocarbanions and dianions. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) using the salts as replacements for LiPF<sub>6</sub> or as additives, in parallel with the control electrolyte with LiPF<sub>6</sub>, to demonstrate improved cycling behavior performance over 200+ cycles. (Sep. 12) **On schedule**
- Prepare/characterize ILs with DFOB<sup>-</sup> and partially fluorinated cyanocarbanions. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) using the salts as replacements for aprotic solvents or as additives, in parallel with the control electrolyte with LiPF<sub>6</sub>, to demonstrate improved cycling performance over 200+ cycles. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

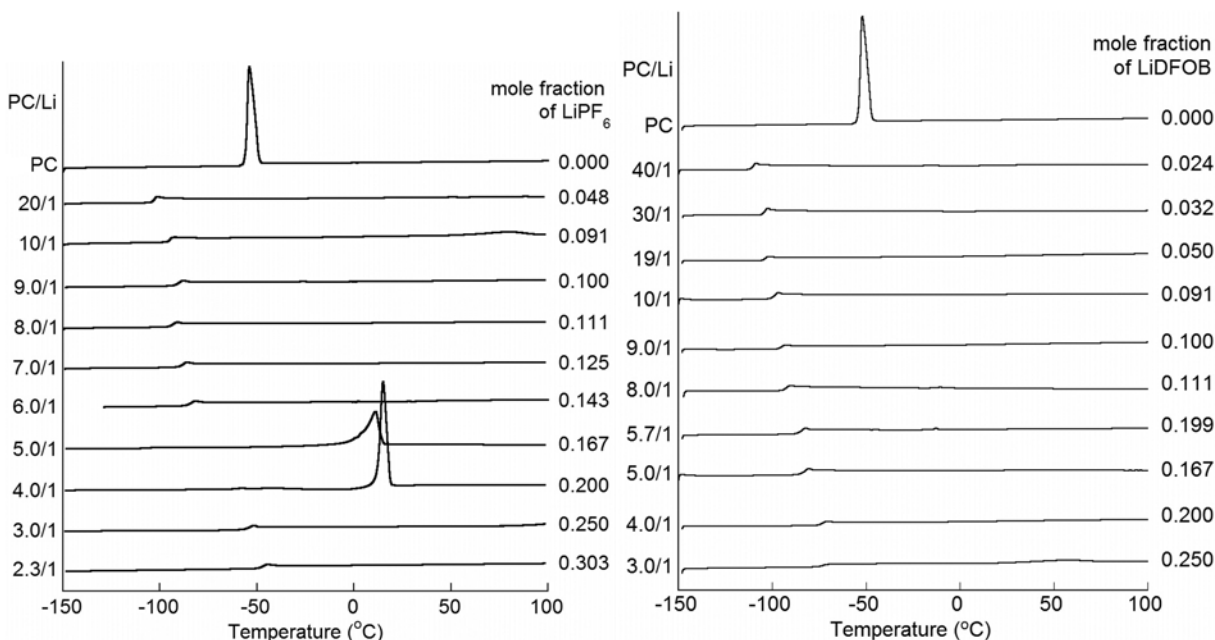
**Phase Behavior/Properties of Solvent-LiX Mixtures:** The phase behavior of  $(\text{EC})_n\text{-LiX}$  and  $(\text{PC})_n\text{-LiX}$  mixtures with  $\text{LiPF}_6$  and  $\text{LiDFOB}$  (lithium difluoro(oxalato)borate) has been determined.  $\text{LiPF}_6$  forms a 4/1 crystalline solvate with uncoordinated  $\text{PF}_6^-$  anions with both EC and PC, as well as GBL. The crystal structure for the  $(\text{GBL})_4\text{:LiPF}_6$  solvate is shown in Fig. 1. With most Li salts, PC does not form crystalline solvates. This is also the case with  $\text{LiPF}_6$ , except for mixtures close to the 4/1  $\text{PC/LiPF}_6$  concentration (Fig. 2).  $\text{LiDFOB}$ , in contrast, does not form any crystalline solvates with either EC or PC (Fig. 2), as is also the case for the mixtures with  $\text{LiFSI}$ . Preliminary work indicates that  $(\text{DEC})_n\text{-LiPF}_6$  mixtures also form a 4/1 solvate phase, although this melts at a lower temperature than for the cyclic carbonates/ester. Transport property measurements for the binary solvent-salt mixtures are underway.

**Anion Synthesis:** The synthesis of  $\text{LiETAC}$  has been successfully scaled up to facilitate the full characterization of the Li salt, as well as the production of ILs. The recently reported salt lithium 4,5-dicyano-2-(trifluoromethyl)imidazolid (LiTDI) has also been synthesized for characterization to facilitate a comparison with lithium dicyanotriazolate (LiDCTA). Initial work suggests that the ions from LiTDI are much less associated in aprotic solvents than is found for LiDCTA. The phase behavior and transport properties for these salts in mixtures with aprotic solvents are also being characterized with the same protocol as for  $\text{LiPF}_6$ ,  $\text{LiFSI}$  and  $\text{LiDFOB}$ .

**Collaborations:** Oleg Borodin and Richard Jow (Army Research Laboratory) and Stefano Passerini (Münster Electrochemical Energy Technology group, University of Münster).



**Figure 1.** Crystal structure of the  $(\text{GBL})_4\text{:LiPF}_6$  solvate (Li-purple, O-red, P-orange, F-green).



**Figure 2.** DSC heating traces of  $(\text{PC})_n\text{-LiPF}_6$  and  $\text{-LiDFOB}$  mixtures.

**TASK 3.8 - PI, INSTITUTION:** Austen Angell, Arizona State University

**TASK TITLE - PROJECT:** Electrolytes – Sulfones with Additives as Electrolytes

**SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Electrolyte needs increased oxidation resistance with decreased ionic resistance, and improved safety. Safety will follow increased ionic liquid or superionic solid content

**OBJECTIVES:** To devise new electrolyte types (sulfone mixtures and superionic glasses or plastic solid derivatives) that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection, and to provide optimized nanoporous supporting membranes for this electrolyte.

**GENERAL APPROACH:** The approach is twofold: (i) A suite of electrolyte studies, beginning with cell-performance testing of recently developed sulfone electrolytes and extending to the design of novel Li<sup>+</sup>-conducting media, are planned. The latter will retain the high oxidation resistance known for noncyclic sulfones, and conductivity of EC-DMC solutions, but will have Li<sup>+</sup> transport number unity. Novel Li<sup>+</sup>-conducting thiophosphate solids (known  $\sigma > 10$  S/cm) and rubbery polymers (developing) will be tested for compatibility with the chosen Li(Ni,Mn) spinel cathode. Finally, some ionic liquid electrolytes will be tested. (ii) The second is the further development of the “Maxwell slats” approach to synthesis of nanoporous supports. A hot water-soluble reversibly-self-assembling net has already been developed as model, and a stronger-bonded model that self-assembles in hot ionic liquid solvents, is the next target.

**STATUS OCT. 1, 2011:** Half-cell and full-cell tests with the Li(NiMn) high voltage cathode using our newly developed graphite-compatible all-sulfone, and part sulfone electrolyte solvents, will have been completed, and relative merits assessed. Tests of fluorinated sulfone FPMS, with DMC co-solvent in similar half-cell and full cell modes will be done. The crystal structures of one of our self-assembling open-network structures (and its pore space fraction) will be known, and the XRD of its nearest glass-forming analog will be available for comparison. Studies to expand the glassy range and mechanical properties will be in progress.

**EXPECTED STATUS SEP. 30, 2012:** A go-no-go point will have been passed on sulfone- solvent-based high voltage cell development. An alternative solvent system of even higher voltage window and comparable conductivity, based on “ionic liquid” solvents, will have been tested for performance with the Li(Ni,Mn)O<sub>4</sub> cathode, and variants of the superionic glass and metastable crystal variety will have been examined. The best cases of the latter will have been tested with the Li(Ni,Mn)O<sub>4</sub> cathode and the expected absence of side reactions verified. The nanoporosity of aqueous self-assembling models of the Maxwell slat concept will have been assessed, and study of more practical (stronger-bonding) variants will have been commenced.

**RELEVANT USABC GOALS:** 1000 cycles (80% DoD); 10 year life. An electrolyte with electrochemical window 5.2 volts and conductivity 20 mS/cm

**MILESTONES:**

- (a) Complete full evaluation of sulfone solvent-based high voltage cells. (Dec. 11) **Complete**
- (b) Complete development of water-soluble self-assembling models of “Maxwell slat” porous solids for creation of self-supporting nanoporous membranes. (Dec. 11) **Complete**
- (c) Complete evaluation of ionic liquid-based, and hybrid, solvent electrolytes. (Apr. 12) **On schedule**
- (d) Test and compare Li(Ni,Mn) spinel cells using ionic liquid-based electrolyte. (May 12) **On schedule**
- (e) Test and compare glass and glass-stuffed polymer electrolyte types in cells. (Jun. 12) **On schedule**
- (f) Develop covalent-bonded equivalents of the self-assembling nets. (Jul. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

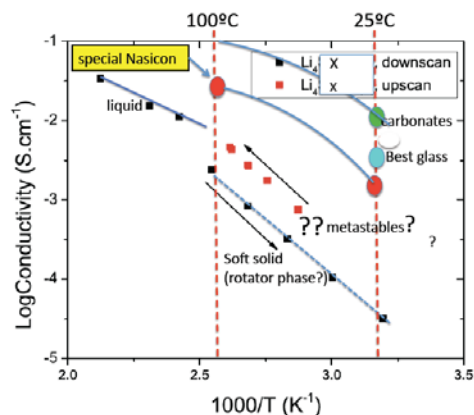
### (a) Complete full evaluation of sulfone solvent-based high voltage cells (concluded).

Excellent graphite anode half-cell performance was reported for particular mixed sulfone based electrolytes in the 2011 2nd quarterly, but was followed by disappointing cathode half-cell results. At first attributed to poor cathode fabrication facilities, the existence of basic problems stemming from cathode-electrolyte reactions was then confirmed by Post-Doc Ueno on return to Japan where state-of-the-art cathode fabrications were possible. While cyclic sulfolane remains a viable choice for cathodes (Amine, ARL), it has been concluded that the pursuit of acyclic sulfone electrolytes should be dropped in favor of (b) and (d) below.

### (b) Complete development of water-soluble self-assembling models of “Maxwell slat” porous solids for creation of self-supporting nanoporous membranes (Dec. 2011)

As reported in the 4<sup>th</sup> quarterly (2011), it has not proven possible to find the appropriate solvent conditions for this self-assembly process to succeed. It was therefore put aside to attempt item (f) below, which was expected to be much more difficult. However, it proved almost immediately successful to the extent that film images and porosity assessments were already reported in the 4<sup>th</sup> quarter of 2011 (see also (f) below)

### (c) Complete evaluation of ionic liquid-based, and hybrid, solvent electrolytes (Mar. 2012)

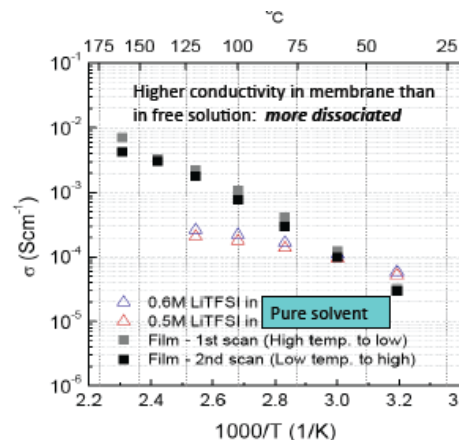


Based on unpublished studies from a previous IL project, research has begun on novel inorganic salts that favor de-trapping of the Li cation from its anion environment to maximize Li mobility. Preliminary conductivity data for the simplest member of a broad family of novel variable valence large-volume quasi-spherical anion Li salts are shown in Fig. 1, where comparison is made with the best available Li-conducting ceramics, glasses, and molecular solvent systems. These systems should have high Li transport numbers and wide electro-chemical windows. Some phases in Fig. 1 may be metastable. Nanoheterogeneous versions have been prepared.

### (d) and (e) Test and compare (on schedule)

### (f) Develop covalent-bonded equivalents of the self-assembling nets by July 2012.

In preliminary studies of this porous glass concept made some years ago, covalent bonds between corner linkers and slats were made by eliminating ethanol from solutions of tetraalkoxy



compounds of titanium and dihydroxy slat compounds, but the products were always powders because of lack of reversibility in the bond formation. Now it has been found that the route to dissolution to viscous liquid forms, which, on solvent removal, exhibit 15 to 20 nm pore structures. When a Li salt, LiNTf<sub>2</sub>, is included in the solvent and a film formed by removing solvent until the film becomes solid, the conductivity can be determined and compared with the value of the free solution. The solvent is poorly dissociating so the conductivity of the free solution is low, Fig. 2. Remarkably, the conductivity of the membrane is higher than the maximum conductivity in the free solution, evidently due to enhanced dissociation in

nanoconfinement, an unexpected and encouraging result. Ways to toughen the film by introducing flexible slats and linear polymer inclusions will be sought.

## **BATT TASK 4**

### **CATHODES**

**Task 4.1 - PI, INSTITUTION:** Michael Thackeray, Argonne National Laboratory

**TASK TITLE:** Cathodes – Novel Cathode Materials and Processing Methods

**SYSTEMS:** Conoco Philips CPG-8 Graphite/1M LiPF<sub>6</sub>+EC:DEC(1:2)/Toda NMC  
Conoco Philips CPG-8 Graphite/High voltage electrolyte/Li-Ni-Mn-O spinel

**BARRIERS:** Low energy, cost and abuse tolerance limitations of Li-ion batteries

**OBJECTIVE:** To develop low cost, high-energy and high-power Mn-oxide-based cathodes.

**APPROACH:** Li<sub>2</sub>MnO<sub>3</sub>-stabilized composite electrode structures, such as ‘layered-layered’ xLi<sub>2</sub>MnO<sub>3</sub>•(1-x)LiMO<sub>2</sub> (M=Mn, Ni, Co), ‘layered-spinel’ xLi<sub>2</sub>MnO<sub>3</sub>•(1-x)LiM<sub>2</sub>O<sub>4</sub> and more complex ‘layered-layered-spinel’ y{xLi<sub>2</sub>MnO<sub>3</sub>•(1-x)LiMO<sub>2</sub>}•(1-y)LiM<sub>2</sub>O<sub>4</sub> systems are receiving international attention because they can provide rechargeable capacities between 200 and 250 mAh/g between 4.6 and 2.0 V vs. lithium. These electrodes suffer from voltage decay and surface instability on cycling, thereby compromising the energy and power of the lithium-ion cells and preventing their implementation in practical systems. A novel, simple and versatile processing technique, using Li<sub>2</sub>MnO<sub>3</sub> as a precursor, to synthesize composite electrode structures is advocated; it offers the possibility of tailoring composite electrode structures and enhancing their electrochemical properties to meet Li-ion battery performance targets for PHEVs and EVs.

**STATUS OCT. 1, 2011:** This is a new project. During the last six months of FY2011, progress was made in exploiting a new synthesis approach in which Li<sub>2</sub>MnO<sub>3</sub> was used as a precursor to fabricate structurally-integrated lithium-metal-oxide composite electrode materials, including ‘layered-layered’, ‘layered-spinel’, ‘layered-rocksalt’ and more complex types. This technique showed promise for stabilizing high capacity (250 mAh/g) lithium-metal-oxide cathodes to cycling over a wide voltage window and, in particular, for combating voltage decay phenomena.

**EXPECTED STATUS SEP. 30, 2012:** Progress will have been made in enhancing the electrochemical and structural stability of ‘layered-layered’ xLi<sub>2</sub>M’O<sub>3</sub>•(1-x)LiMO<sub>2</sub> electrodes at high potentials, with improvements in rate capability and cycle life.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

#### **MILESTONES:**

- (a) Evaluate a new processing route to fabricate stabilized xLi<sub>2</sub>M’O<sub>3</sub>•(1-x)LiMO<sub>2</sub> (‘layered-layered’) electrode structures with a high Mn content using Li<sub>2</sub>MnO<sub>3</sub> as a precursor (Sep. 12) **On schedule**
- (b) Use atomic layer deposition and other methods to stabilize the surface of electrode particles at high charging potentials. (Sep. 12) **On schedule**
- (c) Model surface structures and interfacial phenomena of coated electrodes. (Sep. 12) **On schedule**



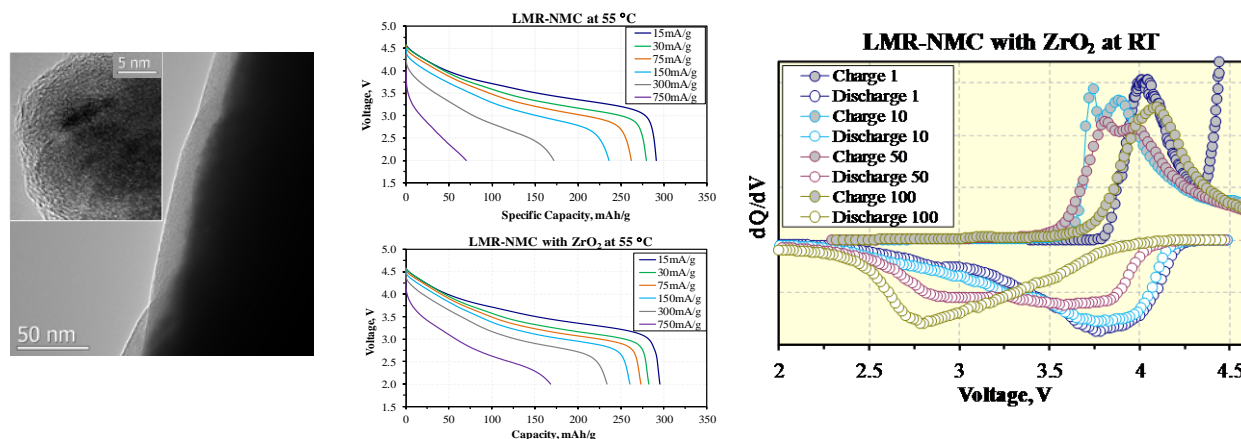
## PROGRESS TOWARD MILESTONES

Collaborators: Swati Pol, Jason Croy, Donghan Kim, Kevin Gallagher, and M. Balasubramanian  
 Milestone (b) addressed: Undertake surface treatments of the electrodes by atomic layer deposition and other methods to stabilize the electrodes at high charging potentials.

Sonication, which makes use of ultrasound energy to stimulate chemical processes in liquids, is being explored as a technique to fabricate thin protective coatings on high-capacity composite electrode structures, such as ‘layered-layered’  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  (e.g., M = Mn, Ni, and Co) to stabilize the surface when the electrodes are electrochemically activated above 4.5 V. Specific objectives of this study are to monitor the effects of sonicated coatings on 1) the rate capability of the electrode, and 2) the voltage decay phenomenon that is known to occur when these electrodes are continuously cycled. A Li- and Mn-rich electrode with composition  $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ , (LMR-NMC) was selected for the study.

Coated electrodes were prepared as follows: A  $\text{ZrO}(\text{NO}_3)$  precursor, dissolved in water with ethanol as co-solvent, was pulse sonicated with pre-dispersed LMR-NMC particles. The slurry was decanted and heated at  $110^\circ\text{C}$  to evaporate the water, followed by heat treatment at  $450^\circ\text{C}$  in air for 2 h. EDS data showed *ca.* 2.6 wt%  $\text{ZrO}_2$  in the coated product, while X-ray dot mapping showed that the  $\text{ZrO}_2$  was uniformly distributed throughout the sample. An HRTEM image indicated that the particles were uniformly coated with *ca.* 20 nm  $\text{ZrO}_2$  layer (Fig. 1).

Uncoated and  $\text{ZrO}_2$ -coated LMR-NMC electrodes were evaluated in Li coin cells using a Li-foil anode and a standard 1.2 M  $\text{LiPF}_6$  in EC:EMC electrolyte. A comparison of the rate capability of cells with uncoated and coated electrodes at  $55^\circ\text{C}$  is shown, respectively, in Fig. 2a and b. While there was no significant change in capacity at the lower rates (15 to 30 mA/g), the rate capability of coated LMR-NMC electrodes was superior at higher rates yielding, for example, *ca.* 170 mAh/g at 750 mA/g, compared to *ca.* 70 mAh/g for uncoated electrodes at the same rate. Despite this improvement, and perhaps not surprisingly, cycling data showed the surface coating did not combat the voltage decay phenomenon, which is associated more with transition metal diffusion within the bulk of the electrode structure (Fig. 3). The change in the voltage profile on cycling the cell 100 times appears to endorse a layered to spinel-like transition with Li insertion occurring over a wide voltage window (approximately 4.0 to 2.5 V) and Li extraction over a much narrower window at high voltages (approximately 3.5 to 4.5 V).



**Figure 1 (left).** HRTEM image of  $\text{ZrO}_2$ -coated LMR-NMC particle with enlarged image of coating.

**Figure 2 (center).** Rate data of Li cells with uncoated electrode (top) and coated electrode (bottom).

**Figure 3 (right).** Voltage profiles of 1<sup>st</sup>, 10<sup>th</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles of a Li/coated LMR-NMC cell.



**TASK 4.3: - PI, INSTITUTION:** Marca Doeff, Lawrence Berkeley National Laboratory

**TASK TITLE:** Cathodes – Design of High Performance, High Energy Cathode Materials

**SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Cost, power and energy density, cycle life

**OBJECTIVES:** To develop high energy, high performance cathode materials including composites and coated powders, using spray pyrolysis and related synthesis techniques.

**GENERAL APPROACH:** High energy cathodes such as modified NMCs and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (LNMS) are synthesized via spray pyrolysis, as well as composites containing these materials, and coated particles. An array of physical and electrochemical techniques are used to characterize their behavior, in conjunction with members of the diagnostics team. Emphasis is placed on increasing energy density without sacrificing stability and cycle life.

**STATUS OCT. 1, 2011:** Phase-pure samples of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> spinel (LNMS) have been produced by spray pyrolysis. Structural characterization of cycled Li[Ni<sub>0.45</sub>Co<sub>0.1-y</sub>Al<sub>y</sub>Mn<sub>0.45</sub>]O<sub>2</sub>; y=0, 0.05 electrodes was completed. Structural and electrochemical characterization of high capacity Li[Ni, Co, Ti, Mn]O<sub>2</sub> compounds will continue.

**EXPECTED STATUS SEP. 30, 2012:** Hierarchically structured LNMS with differing primary and secondary particle sizes will be produced by spray pyrolysis, and optionally provided to interested members of the high voltage spinel discussion group. Work on NMCs will be directed towards understanding the mechanism of improvement in capacities and cycling behavior observed in some compounds when Ti is partially substituted for Co.

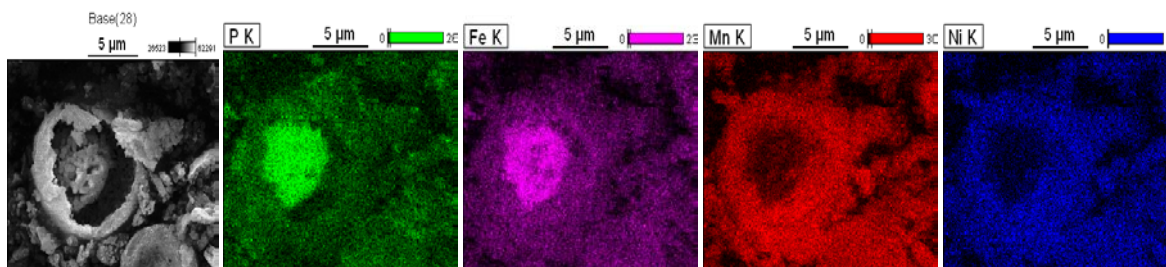
**RELEVANT USABC GOALS:** High energy, thermal stability, cycle life, cost (EV, PHEV).

**MILESTONES:**

- (a) Complete electrochemical characterization of hierarchically structured LNMS made by spray pyrolysis and compare to results obtained on conventional samples and simple particles made by spray pyrolysis. (Sep. 12). **On schedule**
- (b) Make a go/no go decision on Ti-substitution in NMCs as an approach for increasing energy density and improving cycle life. (Sep. 12). **On schedule**

## PROGRESS TOWARD MILESTONES

(1) Initial attempts at spray pyrolysis synthesis of LNMS has only been partially successful so far, due to difficulties controlling the stoichiometry and a tendency to form hollow particles when using the 120 kHz nozzle, which produces particles approximately 10  $\mu\text{m}$  in diameter (solid particles about 1  $\mu\text{m}$  in diameter are formed with the 2.4 MHz nozzle, but it is difficult to produce these materials in quantities sufficient for complete characterization). By infiltrating  $\text{LiFePO}_4$  precursors into the hollow LNMS particles, a composite onion structure was formed, with  $\text{LiFePO}_4$  present on the particle surfaces and in the interior of the shells (Fig. 1). This experiment was performed to illustrate the possibility of making composite structures having a protective or lower voltage material on surfaces of the high voltage LNMS particles to minimize side reactions with electrolytes. Future work will focus on improving control of stoichiometry and morphologies by varying reaction conditions and precursors, the production of coated solid particles and infiltrated composite structures made from hollow particles produced by spray pyrolysis. A comparison will be made to materials made recently by combustion synthesis, which are highly crystalline and show excellent electrochemical behavior. (Collaborations with T. Richardson, J. Cabana, G. Chen, V. Battaglia and other members of the High Voltage Spinel Discussion Group).



**Figure 1.** SEM and EDS mapping images of a broken core-shell particle made by infiltrating a hollow particle of LNMS with  $\text{LiFePO}_4$  precursors followed by calcination. EDS mapping shows that Fe and P are located primarily in the core and outside the shell, while Mn and Ni from the LNMS are confined to the shell.

(2) A paper on Ti-substituted NMCs synthesized by conventional co-precipitation and glycine-nitrate combustion is currently under preparation (with A. Mehta of SSRL). Future work will be directed towards spray pyrolysis synthesis of the most promising materials and characterization to determine the origins of improved capacity and cycling stability.

## PAPERS AND PRESENTATIONS

- 1) “Spray Pyrolysis: Environmentally Friendly Synthesis of High Performance Electrode Materials” Pacific Power Symposium 2012, January 2012, Waikoloa, HI. (invited talk)
- 2) “Spray Pyrolysis Synthesis of Hierarchically Structured Olivine Particles for Battery Applications” Marca M. Doeff, Kinson C. Kam, Thomas Conry, Jun Liu, and Thomas J. Richardson, 7th International Symposium on Inorganic Phosphate Materials, Argonne National Laboratory, November 8-11, 2011.
- 3) “Ultrasonic Spray Pyrolysis of Hierarchically Structured Cathode Materials” Kinson C. Kam, Anthony Chern, and Marca M. Doeff, 220th meeting of the Electrochemical Society, October 2011, Boston MA, Abstract # 604.
- 4) “Characterization of the Effects of Al-Substitution in Layered Oxide Cathode Materials for Lithium-Ion Batteries” Thomas E. Conry, Apurva Mehta, and Marca M. Doeff, 220th meeting of the Electrochemical Society, October 2011, Boston MA, Abstract # 1271.

**TASK 4.4 - PI, INSTITUTION:** Arumugam Manthiram, University of Texas at Austin

**TASK TITLE - PROJECT:** Cathodes – High-capacity, High-voltage Cathode Materials for Lithium-ion Batteries

**BASELINE SYSTEM:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Cost, energy density, power density, cycle life, and safety

**OBJECTIVES:** To develop (i) low-cost cathodes based on polyanions that can offer a combination of high energy and power with excellent thermal stability and safety, and (ii) low-cost, high-voltage spinel cathodes that can offer high power and energy along with long cycle life.

**GENERAL APPROACH:** Focus is on the design and development of cathode materials based on polyanions that have the possibility for reversibly inserting/extracting more than one Li<sup>+</sup> ion per transition metal ion M<sup>n+</sup> and/or operating above 4.3 V. Some example systems to be pursued are Li<sub>2</sub>MSiO<sub>4</sub> and Li<sub>2</sub>MP<sub>2</sub>O<sub>7</sub> (M = Mn, Fe, Co, and Ni). However, there are technical challenges in achieving the theoretical energy densities of many of these cathode materials. Synthesis and processing conditions play a critical role in realizing the full capacities of these polyanion cathodes with more than one Li<sup>+</sup> ion per M<sup>n+</sup> ion. Novel solution-based synthesis approaches such as microwave-assisted solvothermal methods that can offer controlled nanomorphologies are pursued to maximize the electrochemical performances. The synthesized nanostructured polyanion cathodes are characterized by a variety of techniques including *ex situ* and *in situ* XRD, electron microscopy (SEM, TEM, and STEM), X-ray photoelectron spectroscopy (XPS), time of flight – secondary ion mass spectroscopy (ToF-SIMS), and in-depth electrochemical measurements. In addition, the role of cation doping, segregation of certain doped cations to the surface, cation ordering, and morphology on the electrochemical properties of 4.7 V spinel cathodes will be investigated. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships will be developed.

**STATUS OCT. 1, 2011:** Understanding of the self-surface segregation of cations during the synthesis process of high-voltage (4.7 V) spinel oxide cathodes through advanced characterization methodologies, development of novel solution-based synthesis approaches to obtain high-capacity nanostructured polyanion (silicate and phosphate) cathodes, and an investigation of their structure-composition-property-performance relationships.

**EXPECTED STATUS SEP. 30, 2012:** Development of (i) novel synthesis approaches to obtain high-capacity, high-voltage polyanion (silicate and phosphate) cathodes with unique nanomorphologies, (ii) an understanding of the factors that control the performance of high-voltage (4.7 V) spinel oxide cathodes, and (iii) an understanding of their structure-composition-property-performance relationships.

**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles, 10-year life, <20% capacity fade over a 10-year period

**MILESTONES:**

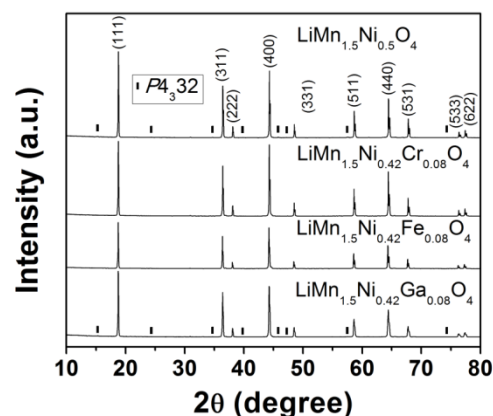
- (a) Understand the role of cation doping, surface modification, and morphology on the electrochemical properties of 4.7 V spinel cathodes. (Dec.11) **Complete**
- (b) Perform surface characterization of LiFe<sub>1-x</sub>Co<sub>x</sub>PO<sub>4</sub> with various x by XPS and ToF-SIMS. (Jun. 12) **On schedule**
- (c) Perform novel synthesis and characterization of Li<sub>2</sub>MSiO<sub>4</sub> and their solid solutions. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

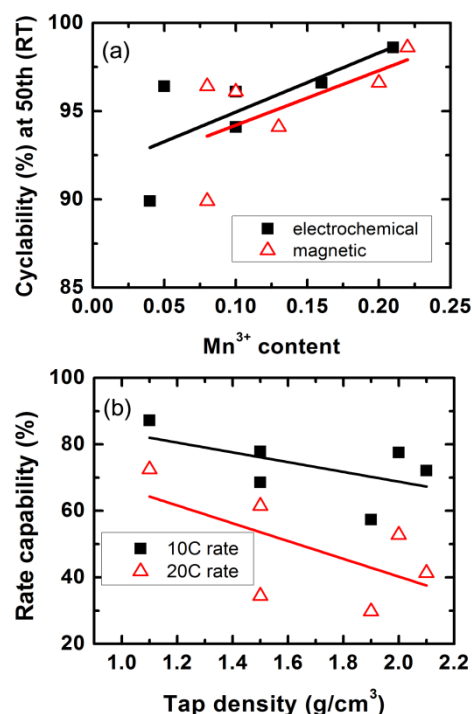
To continue understanding the factors that control the performance of the 4.7 V spinel cathode  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ , focus is on surface segregation, cation ordering, morphology, and  $\text{Mn}^{3+}$  content. A TOF-SIMS study of  $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{M}_{0.08}\text{O}_4$  ( $\text{M} = \text{Al}, \text{Cr}, \text{Fe}, \text{Co}, \text{Zn}$ , and  $\text{Ga}$ ) reveals that Al, Cr, Fe, and Ga segregate to the surface during the synthesis process, while both Co and Zn do not, resulting in a superior performance of the former over the latter. Cation doping also eliminates the  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  impurity phase. In addition, an investigation of the effect of post-annealing at  $700^\circ\text{C}$  of the undoped  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  and doped  $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{M}_{0.08}\text{O}_4$  ( $\text{M} = \text{Cr}, \text{Fe}$ , and  $\text{Ga}$ ) samples synthesized at  $900^\circ\text{C}$  is taking place. While the undoped and Ga-doped samples transform into a more cation-ordered spinel with the  $P4_332$  space group on annealing at  $700^\circ\text{C}$ , as indicated by XRD and FTIR data, the Cr and Fe-doped spinels sustain a high degree of cation disorder even after annealing at  $700^\circ\text{C}$  (Fig. 1). Furthermore, the  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  impurity phase in the undoped  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  sample is eliminated after post-annealing at  $700^\circ\text{C}$ , indicating an increase in the solubility of Ni in the lattice accompanied by a decrease in the  $\text{Mn}^{3+}$  content.

The undoped  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  sample has been studied in various morphologies by different synthesis procedures at  $900^\circ\text{C}$ . The effects of  $\text{Mn}^{3+}$  content, degree of cation ordering, and tap density on cyclability and rate capability have also been investigated. The  $\text{Mn}^{3+}$  contents determined by the capacity in the 4 V region and magnetic measurements agree closely with each other. The samples with different morphologies differ significantly in the  $\text{Mn}^{3+}$  content. The capacity retention at room temperature and  $55^\circ\text{C}$  is proportional to the  $\text{Mn}^{3+}$  content (Fig. 2a). On the other hand, no meaningful relationship was found between cyclability and the degree of cation ordering, as quantified by the intensity ratio of the 588 to  $620\text{ cm}^{-1}$  peak in the FTIR spectra of samples with different morphologies. Also, the rate capability of the undoped sample increases with decreasing tap density (Fig. 2b) due to increasing surface area and does not seem to depend significantly on the  $\text{Mn}^{3+}$  content or the degree of cation ordering.

Future work will focus on understanding various parameters that influence the electrochemical properties of the samples and developing novel synthesis approaches for high-energy phosphate and silicate cathodes.



**Figure 1.** XRD patterns of the  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  and  $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{M}_{0.08}\text{O}_4$  ( $\text{M} = \text{Cr}, \text{Fe}$ , and  $\text{Ga}$ ) samples after post-annealing at  $700^\circ\text{C}$ . The rectangular points indicate the superstructure reflections for the ordered  $P4_332$  space group.



**Figure 2.** (a) Cyclability at the 50<sup>th</sup> cycle vs.  $\text{Mn}^{3+}$  content and (b) rate capability (normalized capacity values at 10 and 20C rates) vs. tap density for the  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  samples with different morphologies.

**TASK 4.5 – PI, INSTITUTION:** Ji-Guang (Jason) Zhang and Jie Xiao, Pacific Northwest National Laboratory

**TASK TITLE:** Cathodes – Development of High Energy Cathode Materials

**BASELINE SYSTEM:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy density, high cost, limited cycle life

**OBJECTIVES:** To develop high-energy, low-cost, and long-life cathode materials.

**GENERAL APPROACH:** Our approach is to develop high-energy cathode materials through a cost effective synthesis process. Appropriate doping, surface treatment and the identification of the electrolytes/additives will be used to improve the electrochemical performance of high voltage LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> based cathode. This high voltage cathode will be further combined with layer cathode to form a composite electrode with ‘layered-spinel’ structure. The experience and technologies developed in the high-capacity composite cathode will be used to further improve the capacity and stability of composite cathode.

**STATUS OCT. 1, 2011:** High-voltage LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> doped with Cr has been synthesized by a facile approach suitable for mass production. The reversible capacity is around 130mAh/g from the doped spinel, which exhibits a stable cycling for more than 100 cycles in half cells. The thermal stability investigation for electrochemically cycled LiMnPO<sub>4</sub> electrodes has been completed. The MnPO<sub>4</sub> reduction to Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> with oxygen evolution was observed only at a temperature higher than 490°C, while the charged MnPO<sub>4</sub> undergoes structure distortion at above 180°C, possibly because of the Jahn-Teller effect accompanied by the decomposition of the passivation film formed on the cathode surface. Investigation of the electrochemical performance of non-stoichiometric LiMnPO<sub>4</sub> will be completed.

**EXPECTED STATUS SEP. 30, 2012:** High-energy cathodes for Li-ion battery applications will be further explored. Using rheological phase reactions that involve only milling and heating processes and are suitable for scale up, layered composite cathodes based on xLi<sub>2</sub>MnO<sub>3</sub>•(1-x)LiMO<sub>2</sub> (M=Mn, Ni, Co, x = 0.3-0.5) will be synthesized and their degradation mechanism will be investigated. The performance of high-voltage spinel LiNi<sub>0.45</sub>Cr<sub>0.05</sub>Mn<sub>1.5</sub>O<sub>4</sub> will also be further improved. Safety, power rate, and cycling stability of these cathode materials will be improved to satisfy the need for HEV/EVs applications.

**RELEVANT USABC GOALS:** >96 Wh/kg (PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

**MILESTONES:**

- (a) Synthesize and electrochemically evaluate Li<sub>2</sub>MnO<sub>3-x</sub> as a baseline. (Mar. 12) **On schedule**
- (b) Utilize rheological phase synthesis of layered composite cathode with 200 mAh/g capacity and stable cycling performance. (Sep. 12) **On schedule**
- (c) Optimize the synthesis approach and inactive components for the high-voltage spinel and composite cathode. (Sep. 12) **On schedule**

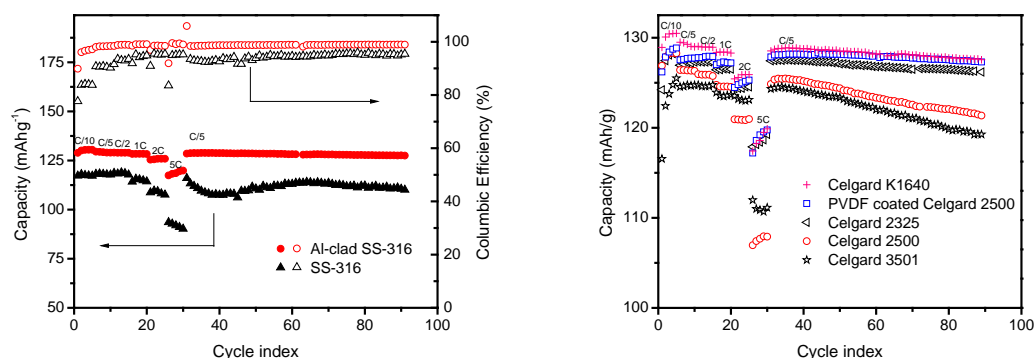
## PROGRESS TOWARD MILESTONES

Most milestones for FY11 have been accomplished. In this quarterly, our systematic investigations on the influences from cell cans and separators on the electrochemical performances of high voltage systems are reported. Major findings for this high voltage system include:

- 1) Aluminum (Al)-clad SS-316 positive-cans have a much better resistance than traditional stainless steel (SS-316) cathode pans to oxidation at high voltages thus improving the initial columbic efficiency of the batteries by more than 13%.
- 2) Polyethylene (PE) separator demonstrates the best electrochemical stability among five different membranes due to its minimal interfacial parasitic reaction with the cathode.

The cycling stabilities of Cr-substituted high voltage spinel ( $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$ ) were compared in SS and Al-clad SS-316 in Fig. 1a. In the commercial SS-316 pans, metal oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  always exist on the surface of cans, which may be corroded by the acidic species (HF) in the electrolyte. Iron and other metal elements in SS-316 will then be exposed to the electrolyte and oxidized during the subsequent charge processes as revealed by XPS spectra. The end result is the reduced efficiency (especially for the first cycle) and increased resistance of the cell. Aluminum-clad SS-316 has a thin but dense layer of alumina covering the stainless steel surface that does not break down when charged at high voltages. With the protection of alumina on cathode pans, reversible capacity, rate, and cycling capability as well as the columbic efficiency are all greatly improved indicating the importance of the treatment on cathode pans for reliable evaluation of high voltage materials.

Figure 1b further compares the performance of the high voltage system using different separators. It was revealed that PE based separator (such as Celgard K1640) is the most stable separator among five different separators investigated for high-voltage spinel cathode materials. The surface reactions between separator and electrolyte at high voltages may lead to undesired deposits on the surface of the separators (XPS data not shown here). Such surface deposits are detrimental to the first cycle efficiency, capacity, rate capability, and long-term cycling stability of the high-voltage Li-ion batteries. The information obtained from those inactive components is useful not only for spinels but also for any other high voltage system.



**Figure 1.** a) Comparison of cycling stability and coulombic efficiency of high voltage spinel by using two different cell pans and b) cycling and rate performances of spinel using different separators. All cells were cycled between 3.0 and 4.9 V at different C rates (1C=147 mA/g).

**Collaborations:** Dr. Kang Xu of Army Research Lab (new electrolyte) and Prof. Whittingham of SUNY Binghamton (magnetic measurements of spinels).

**Task 4.6- PI, INSTITUTION:** Jordi Cabana, Lawrence Berkeley National Laboratory

**TASK TITLE:** Cathodes – Novel and Optimized Phases for High Energy Density Batteries.

**BASELINE SYSTEM:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low-energy-density, poor cycle life, safety

**OBJECTIVE:** Enable higher density Li-ion batteries through an increase in operation voltage and capacity of the cathode. Design electrode structures that maximize active material utilization and charge density. Understand the structure-composition-properties relationship for bulk and surface in electrodes. Identify new compounds containing non-oxide or polyanions in their crystal structure that are electrochemically active.

**GENERAL APPROACH:** Employ and develop a variety of synthetic methods to produce materials with controlled purity, crystal structure and particle morphology. Use spectroscopic and diffraction techniques and controlled materials to get a complete picture of the different reactions involved in battery electrodes. Explore chemical spaces in search for new phases that may provide performance improvements. Establish the importance of the extended electrode structure on electrochemical performance.

**STATUS OCT. 1, 2011:** Samples of LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> with morphology decoupled from the crystal chemistry (Mn<sup>3+</sup> content, Ni-Mn ordering) were successfully synthesized. Annealing of the samples provided control of these parameters. Analysis of their electrochemical properties as battery electrodes revealed that seemingly small variations among samples produce significant effects on electrochemical performance.

**EXPECTED STATUS SEP. 30, 2012:** The composition and crystal structure of the annealed samples of LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> will have been analyzed by coupling spectroscopic tools with diffraction. The role of oxide additives on the performance of spinel electrodes will have been assessed. The first set of new fluoride-containing phases will have been prepared and their applicability as Li battery cathodes will have been established.

**RELEVANT USABC GOALS:** 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

**MILESTONES:**

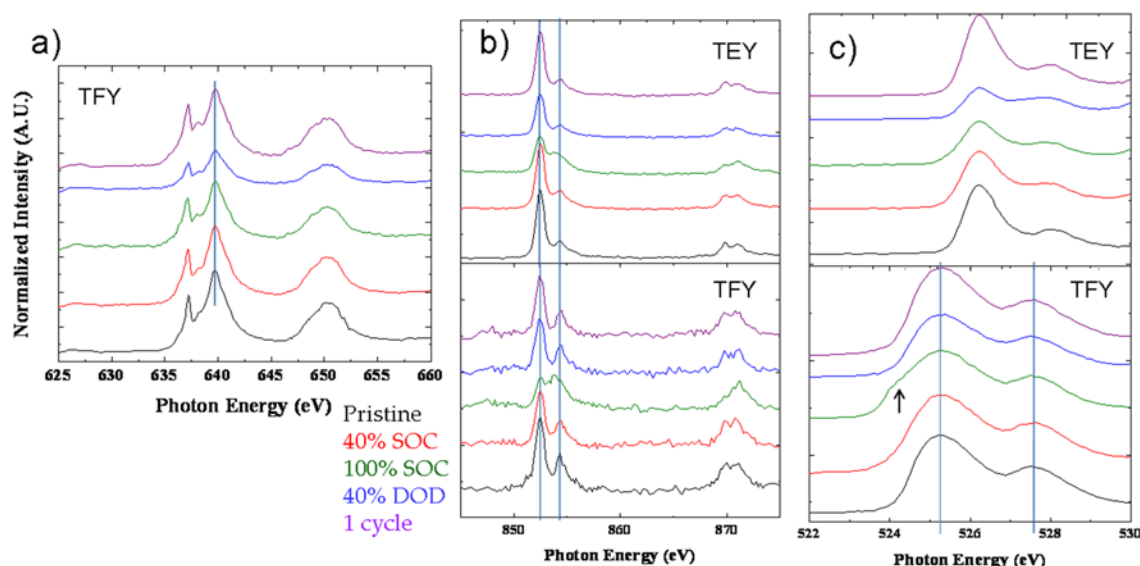
- (a) Complete the crystal-chemical characterization of annealed LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>4</sub> and identify its role on electrochemical performance. (Mar. 12) **On schedule**
- (b) Synthesize and physico-chemically characterize at least two different new phases showing an oxyfluoride network, containing lithium and a light transition metal. (Sep. 12) **On schedule**
- (c) Identify the influence of oxide additives on the extent of electrolyte-electrode side reactions in spinel electrodes. (Sep. 12) **On schedule**



## PROGRESS TOWARD MILESTONES

During the first quarter of FY12, the surface chemistry of pristine and cycled  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  was characterized using soft X-ray absorption spectroscopy at the Ni and Mn  $L_{\text{II, III}}$  and O K edges. The sample was made at 900°C in air. Data from both total electron and fluorescence yield (TEY and TFY) detectors was collected. TEY probes 5 to 10 nm into the electrode, compared to *ca.* 100 nm in TFY mode; therefore, comparisons between surface and bulk species can be traced. Spectra were collected in the pristine state, at 40 and 100% state of charge (SOC), at 40% depth of discharge (DOD), and after 1 full cycle.

A redox process centered at 4 V, amounting to *ca.* 15 mAh/g, was found during charge. This process is associated with the oxidation of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$ . However, the spectra at the Mn  $L_{\text{II, III}}$  edges (Fig. 1a) show no shift or change in line shape, indicating that no changes are detected in the electronic structure of these ions. It is concluded that: i) the total change in redox state for all Mn ions is too small to be detected with these data, and ii) no significant changes occur above 4 V, highlighting the role as formal spectator of these ions. In contrast, the spectra at the Ni  $L_{\text{II, III}}$  edges show notable changes (Fig. 1b). For instance, the 2:1 doublet observed between 850 and 855 eV for the pristine sample turns into a broad 1:1 doublet at 100% SOC. This evolution is correlated with the oxidation of Ni in the compound. However, the doublet in the TEY spectrum at 100% SOC shows a higher peak ratio than in TFY. It is concluded that the surface of the electrode is less oxidized than its bulk. Similar conclusions are reached from the O K edge spectra (Fig. 1c). It can be seen that a shoulder at 524 eV appears on the pre-peak in TFY mode, which is associated with the change in the density of states at the O levels due to the oxidation of Ni. No such shoulder is observed in TEY mode. The fact that less electron depletion is found at the surface of the electrode is taken as indication that the electrode material directly participates in the decomposition of the electrolyte. The very highly acidic species that result from the oxidation of the oxide attack the electrolyte molecules to reduce the oxide to a less unstable state. Work is in progress to verify this hypothesis with surface-coated samples.



**Figure 1.** XAS for  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  at different cycling states, as indicated, at the a) Mn, b) Ni  $L_{\text{II, III}}$ , c) O K edges.

**Task 4.7 - PI, INSTITUTION:** Jason Graetz, Brookhaven National Laboratory

**TASK TITLE:** Cathodes – Novel Materials

**BASELINE SYSTEM:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy density and cost

**OBJECTIVE:** Develop low-cost cathode materials that offer high energy density (>660 Wh/kg) and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.

**GENERAL APPROACH:** Our approach is to develop and utilize specialized *in situ* reactors designed to investigate solvothermal synthesis reactions in real-time using synchrotron techniques. This unique capability will allow us to identify intermediate or transient phases and better control phase nucleation, reaction rates and material properties. These new tools and insights will be used to prepare novel high energy density lithium cathode materials ( $\geq 660$  Wh/kg).

**STATUS OCT. 1, 2011:** This project is a new start. All equipment and plans are in place for the initial project tasks.

**EXPECTED STATUS SEP. 30, 2012:** In Year 1 the existing quartz capillary reactor will be modified to accommodate higher pressures and temperatures. A procedure for the synthesis of LiMBO<sub>3</sub> (M = Mn and/or Fe) will be developed and complete preliminary electrochemical measurements.

**RELEVANT USABC GOALS:** 200 Wh/kg (EV requirement); 96 Wh/kg, 3000 cycles (PHEV 40 mile requirement); lower cost batteries.

**MILESTONES:**

- (a) Complete design and order necessary components for second-generation capillary reactor capable of accommodating higher pressures and temperatures. (Apr. 12) **On schedule**
- (b) Develop a procedure for the synthesis of LiMBO<sub>3</sub> (M = Mn and/or Fe). (Sep. 12) **On schedule**
- (c) Complete preliminary characterization of synthesis reaction(s) using the *in situ* capillary reactor. (Sep. 12) **On schedule**

## **PROGRESS TOWARD MILESTONES**

Efforts in the first quarter of FY12 were focused on recruiting postdocs and students along with setting up equipment. The preliminary chemicals and equipment needed for the project have been procured.

## **BATT TASK 5** **DIAGNOSTICS**

**TASK 5.1 - PI, INSTITUTION:** Robert Kostecki, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics – Interfacial Processes

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low energy (related to cost), poor lithium battery calendar/cycle lifetimes.

**OBJECTIVES:** (i) Establish direct correlations between electrochemical performance of high-energy Li-ion composite cathodes, and surface chemistry, morphology, topology and interfacial phenomena, (ii) improve the capacity and cycle life limitations of Li-alloy anodes

**GENERAL APPROACH:** Our approach is to (i) apply *in situ* and *ex situ* Raman and FTIR far field and near field spectroscopy/microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, electron microscopy (SEM, HRTEM), and standard electrochemical techniques to detect and characterize bulk and surface processes in intermetallic anodes, and high-energy cathodes, (ii) design and apply a new model electrochemical experimental setup to study the kinetics of lithium alloying and diffusion in intermetallic anodes, and possible correlations with the formation and long-term stability of the SEI layer.

**STATUS OCT. 1, 2011:** Insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes is expected to have been gained and their impact on the electrode long-term electrochemical behavior is expected to have been evaluated. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. *In situ* and *ex situ* far- and near-field FTIR and Raman spectroscopy will be employed in conjunction with AFM surface imaging will be applied to detect and monitor surface phenomena at the intermetallic anodes. Similar experimental methodology will be used to detect and characterize surface and bulk processes in high-voltage (>4.3V) model and composite cathodes.

**EXPECTED STATUS SEP. 30, 2012:** The mechanism of electrolyte decomposition at the surface of model anode and cathode materials is expected to be fully understood and its impact on the electrode long-term electrochemical behavior evaluated. The composition and (re)formation dynamics of the surface layer on model monocrystal Sn and Si intermetallic anodes as well as on model single particle and composite high-voltage cathodes will be determined using various complementary spectroscopy techniques. A unique strategy involving the use of *in situ* techniques (AFM, ellipsometry, Raman and fluorescence imaging, FTIR and AP-XPS) in conjunction with *ex situ* techniques (XAS, RBS and NRA) will be applied to monitor and identify surface processes. Preliminary evaluation of near-field optical spectroscopy and imaging techniques for fundamental interfacial studies of Li-ion systems will be carried out.

**RELEVANT USABC GOALS:** *Cycle life:* 5000 (deep) and 300,000 (shallow) cycles. *Available energy:* 96 Wh/kg. *Calendar life:* 15 years.

### **MILESTONES:**

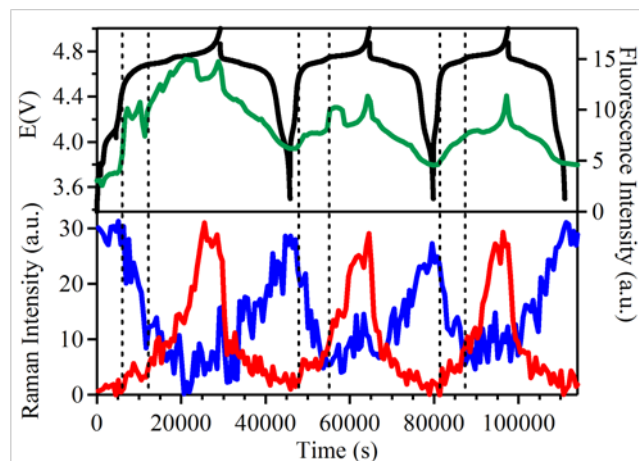
- (a) Resolve SEI layer chemistry of Si and Sn model anodes - collaboration with the BATT Anode Group. (Jul. 12) **On schedule**
- (b) Characterize surface phenomena and bulk phenomena in high-voltage composite cathodes - collaboration with the BATT Cathode Group. (Sep. 12) **On schedule**
- (c) Use near-field IR and Raman spectroscopy to characterize battery materials. (Sep. 12). **On schedule**

## PROGRESS TOWARD MILESTONES

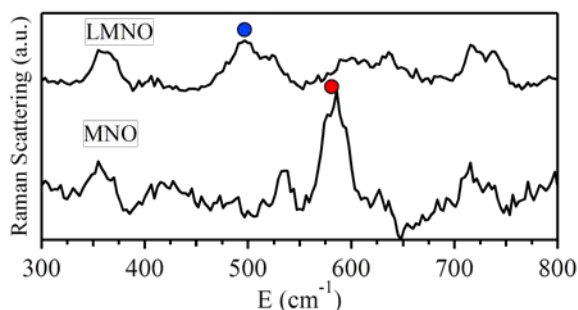
During the 1st quarter of FY12, *in situ* spectro-electrochemical studies of the high-voltage cathode  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel (LMNO) were continued as part of work toward milestone “b”. It was previously demonstrated that *in situ* measurements of fluorescence, which appear as a large background signal in Raman spectra, can be used as a real-time probe for the formation of electrolyte decomposition products on cathode materials. This demonstration has made possible the simultaneous collection of electrochemical, fluorescence, and Raman data on single particles of LMNO in EC:DEC (1:2 w/w) with 1 M  $\text{LiPF}_6$ .

Raman and fluorescence spectra of a single LMNO particle were collected *in situ* while cycling galvanostatically between 3.5 and 5.0 V (Fig. 1). An 80x objective was used on the confocal Raman microscope, which provides localized signal collection near the particle surface and minimizes unwanted contributions from the electrolyte. The electrochemical data (black line) show a small plateau at 4.1 V, as well as two broader plateaus at 4.70 and 4.76 V, which are attributed to the  $\text{Mn}^{3+/4+}$ ,  $\text{Ni}^{2+/3+}$ , and  $\text{Ni}^{3+/4+}$  redox reactions, respectively, of the disordered LMNO spinel. During the charge portion of each cycle, the fluorescence intensity (green line) increases, but not evenly. The most rapid rises during each charge cycle occur approximately at i) the beginning of  $\text{Ni}^{2+}$  oxidation, ii) the beginning of  $\text{Ni}^{3+}$  oxidation, and iii) when the potential approaches 5 V. The *in situ* Raman spectra of LMNO (Fig. 2) show that, after charging, the  $\text{Ni}^{2+}$ -O stretch at  $500\text{ cm}^{-1}$  of lithiated LMNO (blue dot) disappears, and a strong  $\text{Mn}^{4+}$ -O stretch at  $585\text{ cm}^{-1}$  of  $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (MNO-red dot) rises. The integrated intensities of these peaks, presented in the bottom of Fig. 1(a), oscillate during each cycle, with the  $\text{Ni}^{2+}$ -O stretch (blue) beginning to lose intensity at the start of the plateau assigned to the  $\text{Ni}^{2+/3+}$  redox reaction, and the  $\text{Mn}^{4+}$ -O stretch intensity (red) beginning to increase in intensity near the midway state of charge. These trends not only match closely the rise of fluorescence intensity (dashed lines) but also suggest that side reactions that result in the formation of fluorescent species are correlated to LMNO phase transformation processes. In fact, the fluorescence intensity drops at the middle of the 4.76 V plateau, thereby providing evidence that the nascent redox activity of the spinel has a more important role than the cathode potential in the catalysis of electrolyte decomposition. The rise of fluorescence intensity diminishes during subsequent charges, suggesting that the extent of side reactions is reduced, likely due to the formation of a surface layer on the LMNO particle. The increase of coulombic efficiency with cycle number is also consistent with this conclusion.

Progress toward milestones “a” and “c” are on schedule.



**Figure 1.** *In situ* spectroscopy measurements of an LMNO single particle, including the voltage profile of the electrode during galvanostatic cycling (black) and the integrated intensities of the fluorescence (green), the LMNO  $\text{Ni}^{2+}$ -O Raman band at  $500\text{ cm}^{-1}$  (blue), and the MNO  $\text{Mn}^{4+}$ -O Raman band at  $585\text{ cm}^{-1}$  (red).



**Figure 2.** Raman spectra of an LMNO particle from the *in situ* cell before and after the first charge.

**TASK 5.2 - PI, INSTITUTION:** Xiao-Qing Yang and Kyung-Wan Nam, Brookhaven National Laboratory

**TASK TITLE - PROJECT:** Diagnostics – Battery Materials: Structure and Characterization

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** PHEV: Energy density, cycle life; HEV: power density, abuse tolerance

**OBJECTIVES:** To determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density lithium battery with better safety characteristics and longer life.

**GENERAL APPROACH:** To use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft XAS will be used to distinguish the structural differences between surface and bulk of electrodes. Time resolved X-ray diffraction (TRXRD) technique will be used to understand the reactions that occur in charged cathodes at elevated temperatures.

**STATUS OCT. 1, 2011:** Studies on high energy Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> cathode materials during charge-discharge cycling using combined *in situ* hard XAS and *ex situ* soft XAS will be completed. Important information about the roles of Mn cations will be obtained. The *in situ* XAS and XRD studies on mesoporous LiFe<sub>1-y</sub>Mn<sub>y</sub>PO<sub>4</sub> (0.0≤y≤0.8) cathode materials during charge-discharge cycling will be completed. The effects of particle size and morphology on the phase transition behavior and performance of Li-ion cells will be obtained.

**EXPECTED STATUS SEP. 30, 2012:** Structural studies on the high energy density Li<sub>2</sub>MnO<sub>3</sub>-LiMO<sub>2</sub> (M = Ni, Mn, Co) layered materials (in collaboration with ANL) and *in situ* XRD studies on different types of lithium iron phosphate cathode materials with mesoporous structure will be carried out. The diagnostic studies of high voltage LiMn<sub>2-x</sub>M<sub>x</sub>O<sub>4</sub> (M= Ni, Cu etc.) with spinel structure will be completed. Diagnostic studies on high energy density anode materials, such as Si, Sn and alloys will also be conducted.

**RELEVANT USABC GOALS:** 15 year calendar life, <20% capacity fade over a 10-year period, improved abuse tolerance.

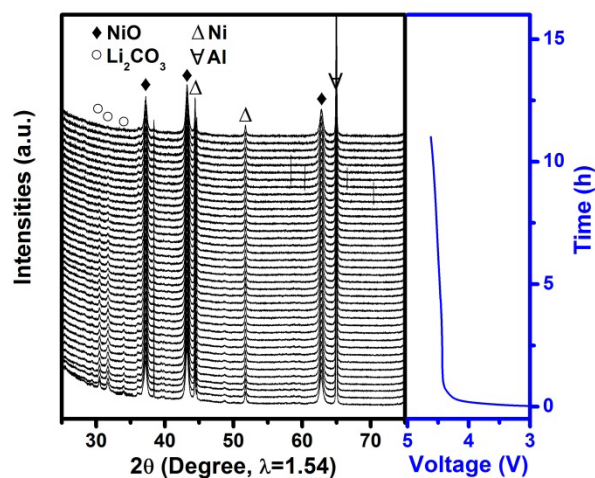
**MILESTONES:**

- (a) Complete *in situ* XRD studies of LiMn<sub>0.4</sub>Fe<sub>0.6</sub>PO<sub>4</sub> cathode material with different particle size and morphology during electrochemical delithiation. (Apr. 12) **On schedule**
- (b) Complete *in situ* XRD studies of Li<sub>2</sub>CO<sub>3</sub> during electrochemical decomposition and the potential application of this process. (Apr. 12) **On schedule**
- (c) Complete *in situ* XAS studies of high voltage LiMn<sub>2-x</sub>M<sub>x</sub>O<sub>4</sub> (M= Ni, Cu etc.) with spinel structure cathode materials during electrochemical cycling. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

In the 1st quarter of FY2012, research at BNL has been focused on the comparative study of the structural changes between  $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$  cathode material samples with different particle sizes and morphology during electrochemical charge-discharge cycling. Progress toward milestones (a) and (b) has been made. In collaboration with Prof. Hong Li and his research group at the Institute of Physics (IOP), Chinese Academy of Sciences (CAS), *in situ* and *ex situ* XRD studies on these two types of materials were carried out. The phase transformation behaviour is quite different for samples synthesized with and without mesopores. The sample without a mesoporous structure undergoes a conventional two-phase reaction starting at the beginning of the first plateau on charge, showing no delay of the phase transition. At the end of charge at 5V, the phase transition to the third phase is not completed. In contrast, for the mesoporous sample, new crystallized phases can only be observed at the end of the first plateau on the charge curve. The transition to the third phase was almost completed by the end of charge at 5.0V. These results show that the phase transition behaviour of  $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$  cathode material is closely related to the morphology of the sample. However, at the same time, the *in situ* XAS results show that the delithiation processes of both materials are synchronized with the electrochemical charge-discharge curve.

For milestone (b), in collaboration with IOP, two types of  $\text{NiO-Li}_2\text{CO}_3$  nanocomposite electrodes have been prepared for electrochemical decomposition studies. A thin film electrode with a thickness of 225 nm and a grain size of around 5 to 8 nm was prepared *via* the pulsed laser deposition method. The powder sample was prepared by a solution evaporation and calcination method with primary particle size in the range of 20 to 50 nm. Using *ex situ* TEM, Raman and FTIR spectroscopy, and synchrotron based *in situ* XRD, the electrochemical decomposition of a  $\text{Li}_2\text{CO}_3$  phase in both types of the  $\text{NiO-Li}_2\text{CO}_3$  nanocomposite electrodes after charging up to 4.1 V vs.  $\text{Li}^+/\text{Li}$  at room temperature is clearly confirmed. This was not found in the electrode containing only  $\text{Li}_2\text{CO}_3$ . The  $\text{NiO}$  phase does not change significantly after the charging process and may have acted as a catalyst for the  $\text{Li}_2\text{CO}_3$  decomposition. The potential of using  $\text{NiO-Li}_2\text{CO}_3$  nanocomposite material as an additional Li source in cathodes of Li-ion batteries has therefore been demonstrated; this could compensate the initial irreversible capacity loss of the anode. As shown in the *in situ* XRD patterns in Fig. 1, during charge, the intensities of characteristic peaks for  $\text{Li}_2\text{CO}_3$  decreased gradually. This confirms that the  $\text{Li}_2\text{CO}_3$  phase is electrochemically decomposed and the  $\text{NiO/Ni}$  phase in the nanocomposite acts as a catalyst for the decomposition reaction.



**Figure 1.** *In situ* XRD patterns of the  $\text{NiO-Li}_2\text{CO}_3$  composite powder electrode.



**TASK 5.3 - PI, INSTITUTION:** Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, Cambridge University

**TASK TITLE - PROJECT:** Diagnostics - First Principles Calculations and NMR Spectroscopy of Electrode Materials

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low rate capabilities; high cost; poor stability; low energy-density

**OBJECTIVES:** Determine the effect of structure on stability and rate capability of cathodes and anodes. Explore relationship between electrochemistry and particle size and shape. Develop new, stable, cathode materials with high energy-density.

**GENERAL APPROACH:** Use solid state NMR and diffraction/TEM to characterize local and long-range structure as a function of particle size, sample preparation method, state of charge and number of charge cycles (cathodes). Use electrochemistry to correlate particle size with rate performance. Continue to develop the use of *in situ* NMR methods to identify structural changes and reactivity in oxides and intermetallics and to examine Li dendrite formation. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure and particle size on cell voltages and rate capability. Use high-throughput computing to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity. Extend to Na systems.

**STATUS OCT. 1, 2011:** *In situ* NMR of silicon and lithium metal anodes, new phosphocarbonates and high voltage cathodes will be ongoing. Several compounds from computational search under experimental investigation.

**EXPECTED STATUS SEP. 30, 2012:** Completed <sup>29</sup>Si studies of lithium silicides and phosphocarbonates. Insights into viability of several Na cathodes.

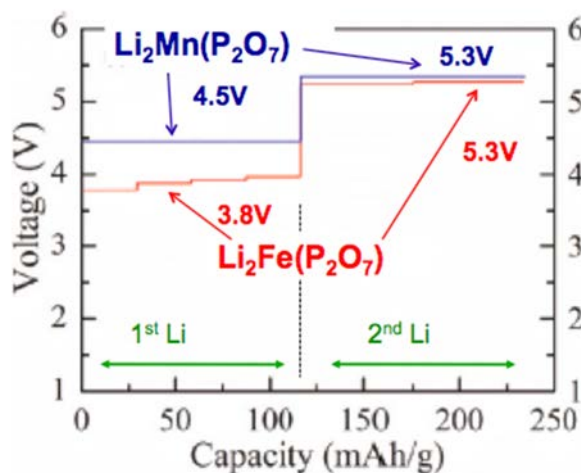
**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, <20% capacity fade

**MILESTONES:**

- (a) Complete <sup>29</sup>Si NMR experiments on crystalline lithium silicides. (Mar. 12) **On schedule**
- (b) Complete electrochemical testing of sidorenkites for Li and Na batteries. (Mar. 12) **On schedule**
- (c) Complete NMR studies of metal doping of LiMnPO<sub>4</sub>. (Mar. 12) **On schedule**
- (d) Complete work on novel intercalation cathode. (Mar. 12) **On schedule**
- (e) Complete <sup>29</sup>Si NMR of amorphous lithium silicide electrodes. (Sep. 12) **On schedule**
- (f) Initiate *in situ* NMR studies of SEI formation on silicon anodes; complete lithium dendrite study. (Sep. 12) **On schedule**
- (g) Suggest at least one new Na intercalation compounds. (Sep. 12) **On schedule**
- (h) Provide computed data on pyrophosphates to Whittingham (Sep. 12) **Complete**

## PROGRESS TOWARD MILESTONES

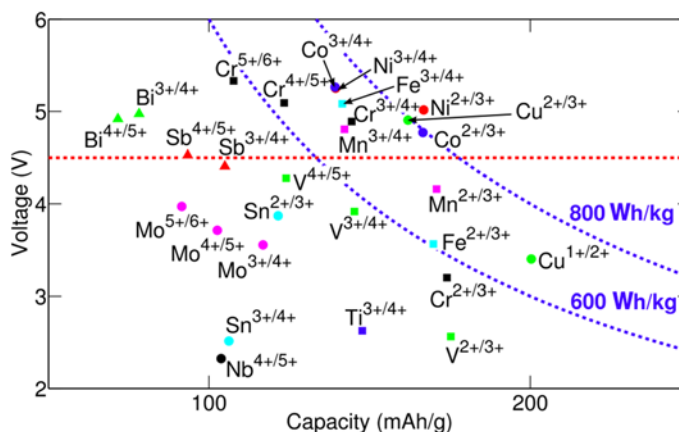
The  $\text{Li}_x\text{FeP}_2\text{O}_7$  and  $\text{Li}_x\text{MnP}_2\text{O}_7$  pyrophosphates have been considered as possible two-electron cathode materials. In a collaboration with Professor Whittingham these materials were evaluated. While the Ceder group has provided computational data, the Whittingham group has



**Figure 1.** Computed voltage profile for Li insertion and extraction from/into  $\text{LiMnP}_2\text{O}_7$  and  $\text{LiFeP}_2\text{O}_7$ .

synthesized and tested the materials. Additional characterization was performed by the Grey group, work in this period focused on the analysis of the pair distribution function (PDF) profile obtained from the X-ray total scattering data of the cycled samples. Figure 1 shows the calculated voltage profile for  $\text{Li}_x\text{FeP}_2\text{O}_7$  and  $\text{Li}_x\text{MnP}_2\text{O}_7$  for  $0 < x < 2$ . Both oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  are feasible, but oxidation to the 4+ state occurs at very high voltage for both Mn and Fe. These predictions indicate that cycling of one Li from  $\text{Li}_2\text{FeP}_2\text{O}_7$  and  $\text{Li}_2\text{MnP}_2\text{O}_7$  will be possible, but the second Li cannot be removed with any current electrolytes.

This is consistent with experimental work performed by the Whittingham group. This work was published in Chemistry of Materials 2011. These findings are consistent with the general trends observed in phosphates. Using calculations on several thousand real and hypothetical phosphate compounds we have been able to datamine the average potential for every possible redox couple. The result is shown in Fig. 2. The results indicate that while in general, the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple are in a reasonable voltage range, the  $\text{Fe}^{3+}/\text{Fe}^{4+}$  couple is very high in voltage. The  $\text{Mn}^{3+}/\text{Mn}^{4+}$  is marginally accessible in some phosphates, but clearly not in the pyrophosphate. The dependence of redox voltage on structure was investigated in more detail as well (not shown).



**Figure 2.** Average computed voltage for redox couples in phosphates.

**Task 5.4 - PI, INSTITUTION:** Yang Shao-Horn, Massachusetts Institute of Technology

**TASK TITLE - PROJECT:** Diagnostics - Studies and Design of Chemically and Structurally Stable Surfaces and Structures of Lithium Storage Materials

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Inadequate energy, and abuse tolerance of Li-ion batteries

**OBJECTIVES:** To develop high-energy and long-cycle-life cathodes.

**GENERAL APPROACH:** Efforts will be focused on exploring the use of lithium peroxides and oxides in the positive electrodes to provide significant enhancement in gravimetric energy relative to conventional lithium interaction compounds. Of particular interest is to examine the influence of catalysts on the charging voltage of such high-energy electrodes. The surface chemistry, microstructure of oxide-electrolyte interface, and oxide crystal structure of high-energy positive electrodes will be examined by a range of techniques such as transmission electron microscopy, synchrotron X-ray diffraction, Raman spectroscopy and X-ray adsorption spectroscopy, and X-ray photoelectron spectroscopy. These surface and structural features and their changes during electrochemical measurements would provide insights into developing strategies in the design of high-energy and long-cycle-life cathodes.

**STATUS OCT. 1, 2011:** Select (Li<sub>2</sub>O<sub>x</sub>)<sub>y</sub>MO<sub>z</sub> electrodes will be prepared and tested in two-electrode and three-electrode cells having lithium as the negative electrode, where the activity of MO<sub>z</sub> such as MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> for Li<sub>2</sub>O<sub>x</sub> oxidation will be compared with that of the state-of-art precious metal catalysts such as Pt/C.

**EXPECTED STATUS SEP. 30, 2012:** The influence of some metal oxide catalysts on the charging voltage of such high-energy electrodes has been established and compared with Pt/C. Changes in the microstructure and crystal structure of select (Li<sub>2</sub>O<sub>x</sub>)<sub>y</sub>MO<sub>z</sub> electrodes have been identified by scanning or transmission electron microscopy and X-ray diffraction. Application of fundamental insights to design of new and stable surfaces for high-energy cathodes will be ongoing.

**RELEVANT USABC GOALS:** High Energy/Power Ratio Battery, energy density (>100 Wh/kg), power density (>400 W/kg), 15-year calendar life and cycle life (5,000 cycles).

**MILESTONES:**

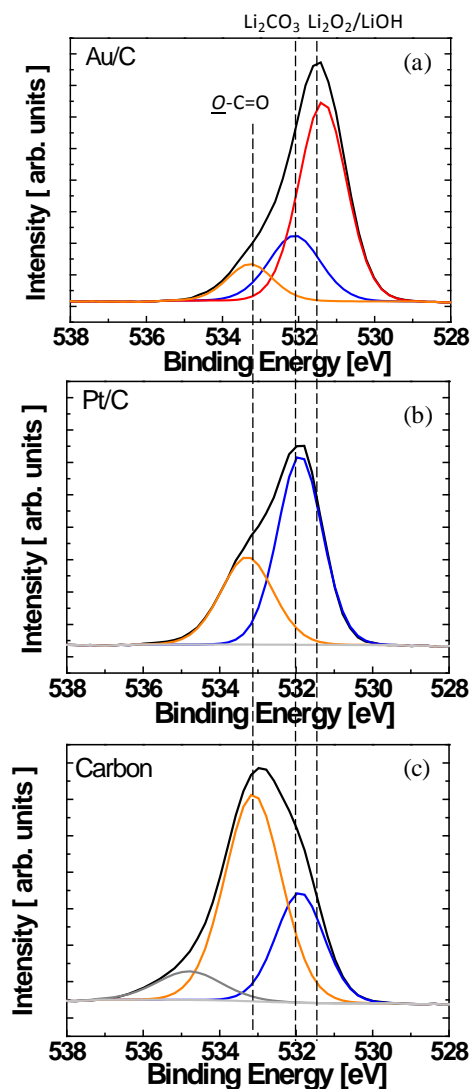
- (a) Complete XPS analysis of the surface chemistry changes of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cycled to two voltages and compare with the surface chemistry changes of Li<sub>x</sub>CoO<sub>2</sub> and LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>. (Jun. 12). **On schedule**
- (b) Demonstrate the oxide catalyst influence on the capacities, discharge/charge voltages or cycle life of (Li<sub>2</sub>O<sub>2</sub>)<sub>x</sub>(MO<sub>2</sub>)<sub>y</sub> (where M = Mn, Co, Ni, etc.) in lithium cells. (Jun. 12) **On schedule**
- (c) Supply XPS and TEM data demonstrating the surface chemistry and morphological changes of (Li<sub>2</sub>O<sub>2</sub>)<sub>x</sub>(MO<sub>2</sub>)<sub>y</sub> during charge and discharge. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

Examining the surface chemistry and the composition of discharge products of cathodes in Li-O<sub>2</sub> cells is vital to fundamentally understanding how catalysts influence the growth of discharge products associated with the Li-O<sub>2</sub> electrochemical reaction. Lab X-ray based XPS (Al K<sub>α</sub> X-rays) has been used to identify the discharge products from oxygen reacting electrochemically with Li ions on the carbon surface, where all samples were transferred from an Ar-filled glovebox to the test chamber of the spectrometer without exposure to ambient conditions. Based on previously reported binding energies for the O 1s region, the discharge products can be assigned mostly to Li<sub>2</sub>O<sub>2</sub> from Li-O<sub>2</sub> cells with a DME-based electrolyte.

In an effort to increase the depth of the region analyzed by XPS, the synchrotron radiation on beamline X24A at NSLS has been utilized and the spectra was collected utilizing monochromatic X-rays with energy of 2555 eV compared to conventional Al K<sub>α</sub> X-rays with energy of 1487 eV. In addition, the synchrotron data was collected at an electron takeoff angle of 85° compared to 45° for conventional data (with respect to the electrode surface). In this way, the depth of the analyzed region increased from *ca.* 5 to *ca.* 13 nm for photoelectrons associated with the O 1s region. The surface chemistry of air electrodes containing pure Vulcan carbon (VC), 40 wt% Au/C (Au/C), and 40 wt% Pt/C (Pt/C) was investigated. All samples were discharged at 100 mA/g<sub>carbon</sub> in 0.1M LiClO<sub>4</sub> in DME with a lower voltage limit of 2 V. They were analyzed in the discharged state and not washed. The O 1s spectra (Fig. 1) show that Li<sub>2</sub>CO<sub>3</sub> at *ca.* 532.0 eV was detected in all electrodes. This might be due to the short time exposure of the air electrodes to ambient prior to XPS data collection. Note that Li<sub>2</sub>CO<sub>3</sub> was not observed with lab-XPS when samples were transferred to the XPS test chamber from an Ar-filled glovebox without exposure to ambient. In addition to clear evidence of Li<sub>2</sub>O<sub>2</sub> (~531.2 eV based on Li<sub>2</sub>O<sub>2</sub> reference powder performed with lab-XPS), a high binding energy component associated with O-C=O (~533.5 eV) was also observed for all electrodes. This study shows the surface chemistry sensitivity of Li-O<sub>2</sub> battery reaction products to air exposure, and highlights the importance of *in situ* techniques to analyze reaction products.

**Collaborations:** Collaborations with Dr. A. Mansour at the NSWC for XPS and XAS measurements through a subcontract of MIT would like to be continued. Collaborations will continue with M.M. Thackeray in using TEM and XPS to study the atomic structure and surface chemistry of composite materials.



**Figure 1.** Synchrotron X-ray XPS spectra of the O 1s photoemission line for discharged (a) Au/C, (b) Pt/C and (c) VC electrodes.

## **BATT TASK 6**

### **MODELING**

**TASK 6.1 - PI, INSTITUTION:** John Newman, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Modeling - Improved Electrochemical Models

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Poor transport properties, capacity and power fade

**OBJECTIVES:** Develop experimental methods for measuring transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

**GENERAL APPROACH:** Use simulations to improve understanding of limitations in cell performance. Develop improved experimental methods for measuring transport and kinetic properties.

**STATUS OCT. 1, 2011:** Experiments measuring the kinetics of ferrocene reduction through a passivating film on glassy carbon will be complete. Characterization of the SEI on highly-oriented-pyrolytic graphite (HOPG) will be ongoing. Comparison of ferrocene kinetics in the presence and absence of additives will be ongoing.

**EXPECTED STATUS SEP. 30, 2012:** Characterization of the SEI on HOPG will be complete. Comparison of ferrocene kinetics in the presence and absence of additives will be complete. A model for the formation of the SEI will be complete.

**RELEVANT USABC GOALS:**

300,000 shallow discharge cycles  
15 year calendar life

**MILESTONES:**

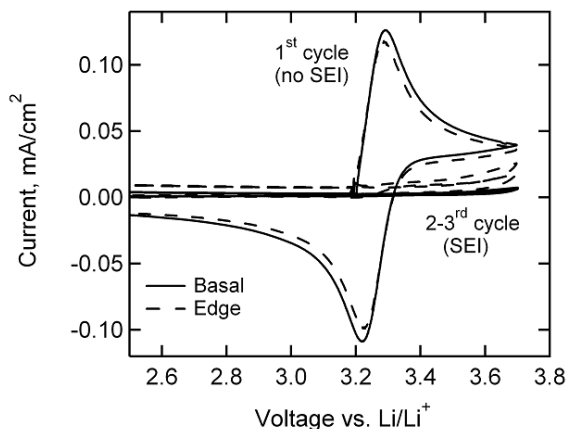
- (a) Obtain AFM and ferrocene kinetic measurements of SEI on HOPG. (Dec. 11).  
**Complete/canceled**
- (b) Compare through-film ferrocene kinetics for SEI formed in presence of VC and FEC. (Apr. 12) **On schedule**
- (c) Develop model to explain current-time curves for film formation. (Aug. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

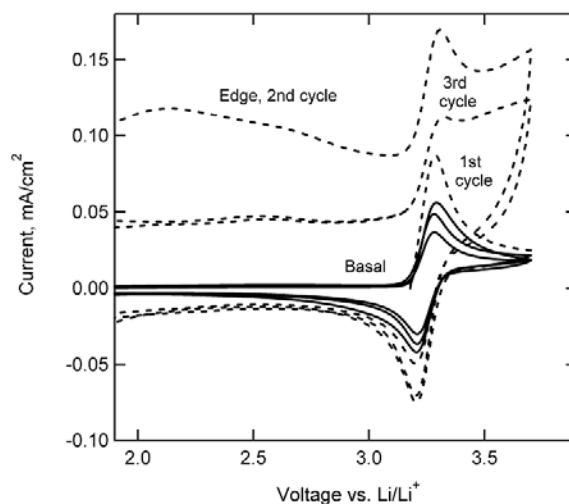
In FY 2011, techniques and models were developed for using ferrocene to characterize the SEI formed on glassy carbon at 0.6 V vs.  $\text{Li/Li}^+$ . Our current task is to use these methods to characterize the SEI formed in different electrolytes and on different surfaces. In Summer 2011, a collaboration began with the Abe group at Kyoto University to study the SEI formed on highly-oriented-pyrolytic graphite (HOPG) instead of glassy carbon. **Because of time and equipment constraints, plans for *in situ* AFM measurements in Milestone (a) were canceled. However, the other half of Milestone (a), obtaining through-film ferrocene kinetic measurements on HOPG, was completed.** A paper on this subject was submitted to the Journal of the Electrochemical Society and is currently under review. A comparison of SEI formation and electrode passivation on the edge and basal plane of HOPG in both  $\text{LiClO}_4$ -based and  $\text{LiPF}_6$ -based electrolytes was made. Cells were cycled from open circuit to 3.7 V, then to 0.1 V vs.  $\text{Li/Li}^+$  at 20 mV/s. Approximately 2 mM ferrocene was also added to the electrolyte in order to monitor the degree of electronic passivation at the surface. SEI formation current (not shown) is higher on the edge than the basal plane, in agreement with expectations. This result is true for both electrolytes, although the magnitude and location of peaks are different.

Figure 1 shows the effect of the SEI on ferrocene oxidation and reduction in  $\text{LiClO}_4$ -based electrolyte. Before SEI formation and after correcting for ohmic drop, the response is almost reversible. After only one cycle of formation, the CV shows almost no ferrocene oxidation and reduction on the basal plane, and a very small current on the edge plane. Thus, the SEI formed on both orientations is almost completely electronically passivating after the first cycle.

Results for  $\text{LiPF}_6$ -based electrolyte are shown in Fig. 2. On the basal plane (solid line), the peak ferrocene oxidation and reduction currents decrease slightly with each cycle, and the peak potential separation remains nearly constant. Thus, passivation is much slower than in  $\text{LiClO}_4$ -based electrolyte. The edge plane shows a large oxidation current, even below 2.0 V on the second cycle, peaking at 2.1, 3.25, and 3.7 V. Because the peak current at 3.25 V is higher than that observed with no SEI, the oxidation current must correspond to oxidative stripping of SEI products from the electrode. Removal of SEI products explains why the reduction peak for ferrocenium on the second cycle is almost unchanged from that on the electrode without an SEI. As the electrode is cycled a third time, the decreased heights of the oxidation and reduction peaks show that the ferrocene reaction is suppressed. Our current task is to explore in more detail the oxidative stripping reactions to explain why they occur only in  $\text{LiPF}_6$  and not  $\text{LiClO}_4$  solutions.



**Figure 1.** Ferrocene characterization,  $\text{LiClO}_4$  electrolyte



**Figure 2.** Ferrocene characterization,  $\text{LiPF}_6$  electrolyte

**TASK 6.2 - PI, INSTITUTION:** Venkat Srinivasan, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Modeling – Model Experimental Studies on Next-generation Li-ion Battery Materials

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** Low calendar/cycle life; Low energy, High cost

**OBJECTIVES:**

1. Quantify power limitations in porous cathodes and its relationship to design.
2. Develop a model to account for porosity in electrode secondary particles and quantify effect on performance
3. Develop a model for mechanical degradation of electrodes with consideration of particles and binder.

**GENERAL APPROACH:** Develop mathematical models for candidate Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to connect fundamental material properties to performance and degradation modes and provide guidance to material-synthesis and cell-development PIs. Use models to quantify the ability of the candidate chemistry to meet DOE performance goals.

**STATUS OCT. 1, 2011:** A preliminary model that quantifies the importance of incorporating binder effects in predicting failure of particles will be complete. The impact on low volume change systems like graphite and high volume change systems like silicon will be examined. The rate capability of NCM cathodes on a particle scale will be quantified and the relevant transport properties measured.

**EXPECTED STATUS SEP. 30, 2012:** The performance models for Si anode with the NMC cathode will be complete and comparison made with the baseline. The degradation of graphite and candidate alloy anodes that takes into account the interaction of the active material and the binder will be complete. A model that accounts for the reaction distribution across the electrode will be developed and compared to experimental data.

**MILESTONES:**

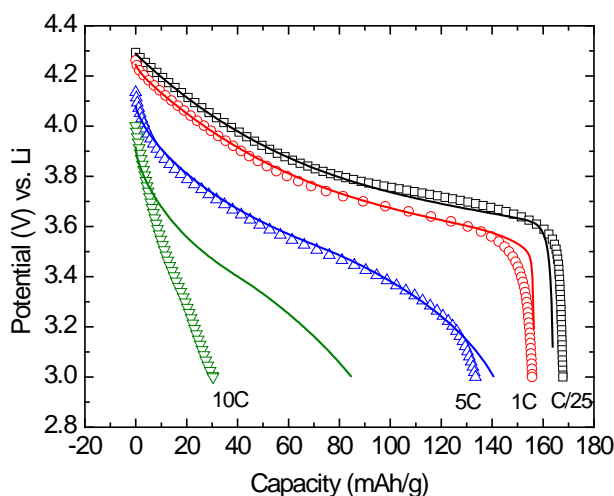
- (a) Construct a silicon anode particle model that incorporates a coupling between kinetics and stress during lithiation and delithiation. (Feb. 12) **On schedule**
- (b) Compare the porous electrode model with experimental data of NCM cathode and quantify effect of porosity and conductive aids on performance. (Mar. 12) **On schedule**
- (c) Develop a model for porous particles applying to Ni/Mn spinel oxides and report on the effects of secondary particle porosity on battery performance. (Sep. 12) **On schedule**
- (d) Couple the particle model with a model of the surrounding binder material to quantify the effect of binder properties on damage to the binder and binder-particle interface. (Sep. 12) **On schedule**



## PROGRESS TOWARD MILESTONES

**Modeling NMC Cathode:** In the last quarter it was shown that NMC particles could be charged and discharged at rates exceeding 100C. These high rates, previously not reported, are observed in electrodes specifically made very thin in order to eliminate porous electrode effects. These results suggest that limitations in this system occur on the porous electrode scale, rather than on the particle scale.

In this quarter, the system limitations at the electrode scale were studied by using the macro-homogeneous model developed by Newman and coworkers. In the solution phase of the porous electrode, the transport properties of the electrolyte are affected by the porous geometry of the electrode, namely the porosity and tortuosity, which in turn leads to a reaction distribution across the electrode. The Bruggeman relation, which is often used to relate the porosity and tortuosity of the porous electrode, was first examined to explore the diffusion limitation in the solution phase. The typical value of the Bruggeman coefficient used in the literature is 1.5. The simulation obtained using this value was unable to fit the experiment results at a discharge rate above a rate of 1C. Increasing the value from 1.5 to 5.5, which leads to a smaller effective conductivity and ionic diffusion coefficient, resulted in model fits that were comparable to experimental data up to 5 C (Fig. 1). However, the model was unable to predict the results at 10 C.



**Figure 1.** Model-experimental comparisons at various discharge rates. The experimental data (dots) was obtained on a NMC electrode with a thickness of 88  $\mu\text{m}$ . The calculated potentials (lines) were obtained using the Bruggeman coefficient of 5.5.

While the simulations are unable to provide an adequate fit to the experiment at all rates, results to date suggest that at relevant electrode thickness, the solid phase transport limitations are negligible and the electrolyte phase dominates losses. Future work will continue investigating the effects of reaction distribution and transport of Li ions in the tortuous pores in order to accurately predict electrode behavior, especially at rates exceeding 10 C.

**Modeling Mechanical Degradation of Electrodes:** A model has been developed that accounts for the effect of large deformation stress in the Butler-Volmer kinetic expression. This modified kinetic expression will be incorporated into a mechanical model of a spherical particle to satisfy the Feb 2012 milestone.

**TASK 6.3 - PI, INSTITUTION:** Ann Marie Sastry, University of Michigan

**TASK TITLE - PROJECT:** Modeling – Thermo-electrochemistry, Capacity Degradation, and Mechanics with SEI Layer

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIER:** Prediction of capacity and power degradation, and excessive additive materials which penalize energy and power density and increase cost.

**OBJECTIVES:** (i) multiscale FE modeling considering phase transition and the mismatch between active material and SEI layer, (ii) simulation in Li-ion batteries including microscale features, (iii) measurement of mechanical properties (*i.e.*, Young's modulus and thickness) of the SEI layer

**GENERAL APPROACH:** Parallel numerical and experimental approaches to study the interrelationships of the solid electrolyte interphase and lithium manganese oxide will be used. The numerical approach will rely upon voxelation of real particle geometries and the finite element technique to solve the complex multiphysics problem of the electrochemical, mechanical and thermal aspects of the SEI layer. Experimentally, the composition, morphology, and physical and electrochemical properties of the SEI using ATR-FTIR, TEM, and AFM, as well as electrochemical techniques to measure the diffusivity and conductivity of the SEI layer will be measured.

**STATUS OCT. 1, 2011:** A multiscale FE model considering particle aggregation, its effect on cathode structure, and the effect in turn on cathode dissolution has been established. An SEI layer formation model and parametric studies for different electrochemical systems have also been established. Finally, experimental techniques (*ex-situ* and/or *in-situ*) will be applied to validate the SEI layer formation model. With these three objectives completed, capacity degradation of Li-ion batteries can be correlated to the properties of SEI layers and particle microstructures.

**EXPECTED STATUS SEP. 30, 2012:** To have (1) applied finite element methods to the phase change/intercalation interrelationship to graphitic anodes, (2) applied numerical techniques to the modeling of the SEI layer on complex electrode geometries, and (3) verified the model using experimental data collected on the physical properties of the SEI layer.

**RELEVANT USABC GOALS:** *Available energy for CD mode:* 3.4 kWh (10 miles) and 11.6 kWh (40 miles); *Cycle life:* 5000 cycles (10 miles) and 300,000 cycles (40 miles); *10- s discharge power:* 45 kW (10 miles) and 38 kW (40 miles); *Calendar life:* 15 years (40°C).

**MILESTONES:**

- (a) Implement multiscale modeling for stresses in active material considering SEI layer. (Mar. 12) **On schedule**
- (b) Couple the 1D electrochemical model with a previously developed micro scale model. (May 12) **On schedule**
- (c) Quantify variation in the mechanical properties of the SEI layer as a function of cycle number. (Aug. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

### 1) Intercalation- and Misfit-Induced Stress in the Graphite Electrodes

Stress/fracture analysis was conducted to evaluate the effect of the SEI layer on stress level in active materials and crack propagation in the SEI layer. Figure 1A shows that the stress intensity factor increases as the crack thickness increases. Also, the crack can propagate through the SEI thickness before being arrested at the interface. At this point, a connected channel can be created. Fig. 1B shows the channeling criteria. The lines represent relative  $K_{IC}$  values to  $2 \text{ MPa} \cdot \text{m}^{-1/2}$  (a) 1.15 (b) 1.12 (c) 1.10 (d) 1.05.

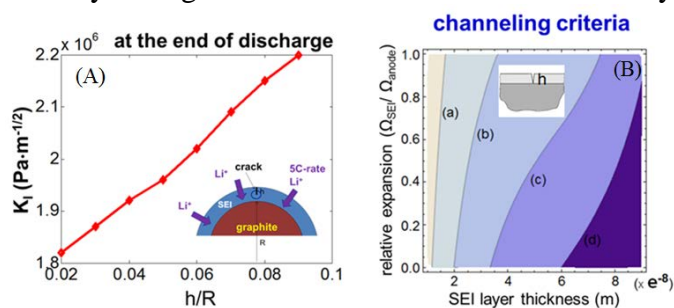


Figure 1.

### 2) Multiscale modeling with self-assembly and dissolution

A numerical simulation based on the variational multiscale approach was conducted to investigate both macro and micro scale phenomena in a Li-ion battery (Fig. 2A). The cell voltage curve with microscopic Li concentrations in the electrolyte shows a transition from reaction-controlled kinetics to diffusion-controlled kinetics (Fig. 2B). These results suggest that stronger reactions on the particle surfaces result from increases of the particle surface area—an attractive idea for increasing battery cell performance.

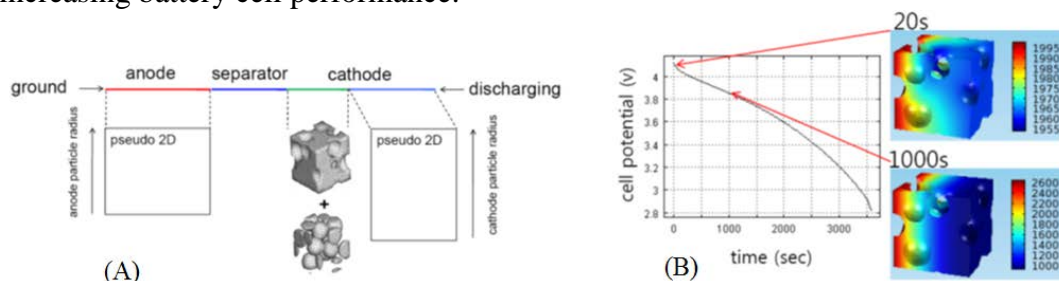


Figure 2.

### 3) Characterization of SEI layers

The effect of the cathode surface layer on Mn dissolution was investigated using inductively coupled plasma (ICP) measurement. Different surface layers were formed on the cathodes by soaking the cathodes in the electrolyte with different additives over the course of three days. Then, the samples were immersed into 1M EC/DMC(1:1) electrolyte during three days at 50°C. As shown in Fig. 3, a similar amount of the Mn dissolution was observed during the period of the surface layer formation. However, the cathode with VEC-derived surface layer showed relatively high Mn dissolution compared to the cathode with the normal surface layer. Mn dissolution of the cathode with FEC-derived surface layer was relatively low. This result suggests that the cathode surface layer may affect Mn dissolution.

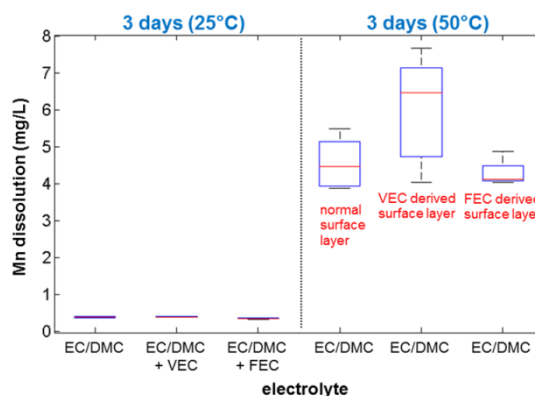


Figure 3.

**TASK 6.4 - PI, INSTITUTION:** Kristin Persson, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Modeling – Predicting and Understanding New Li-ion Materials Using *Ab Initio* Atomistic Computational Methods

**BASELINE SYSTEMS:** Conoco Philips CPG-8 Graphite/1 M LiPF<sub>6</sub>+EC:DEC (1:2)/Toda High-energy layered (NMC)

**BARRIERS:** High cost, low energy, low rate, poor cyclability.

**OBJECTIVES:** 1) Predict new chemistries and crystal structures for improved electrodes as defined by the goals of USABC. 2) Understand diffusion-limiting behavior in current and novel electrode materials in order to suggest chemical or morphological improvements. 3) Understand surface interactions in electrode materials to optimize stability and kinetics.

**GENERAL APPROACH:** Use computational *ab initio* atomistic modeling methods to understand current Li-ion battery electrode materials and use this knowledge to suggest improvements as well as new electrode materials. Use statistical mechanics models to understand Li diffusion in bulk and on surfaces. Combine and make efficient access to all relevant calculated knowledge in a searchable database, facilitating computational materials design.

**STATUS OCT. 1, 2011:** Evaluation of Al substitution effect on LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3-x</sub>Al<sub>x</sub>O<sub>2</sub> in terms of Li mobility and electronic conductivity has been concluded. The study of Li absorption on graphene and multi-layer graphene surfaces will be underway. The Li and cation interactions in LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>2</sub> will be understood as a function of Li content. The materials genome web site is launched from LBNL.

**EXPECTED STATUS SEP. 30, 2012:** Li kinetics on graphene and multi-layer graphite is concluded. Electronic structure studies of surface facet stability of electrode materials (LiMnO<sub>2</sub> and LiFePO<sub>4</sub>) will be underway. Phase diagram of LiNi<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>2</sub> will be concluded. The study of Li kinetics and electronic structure of Li<sub>x</sub>Ni<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>2</sub> as a function of Li content will be underway.

**RELEVANT USABC GOALS:** PHEV: 96 Wh/kg, 5000 cycles; Operating charging temperature: -30 to 52 °C

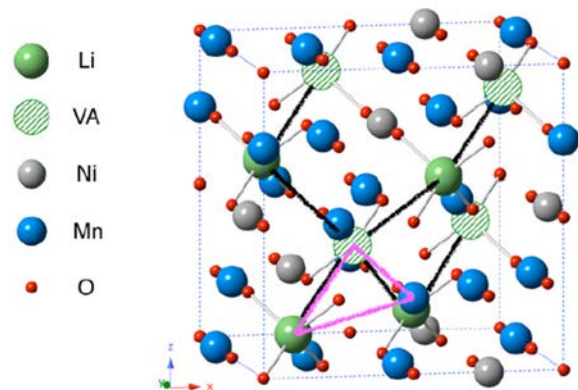
**MILESTONES:**

- (a) Go online with the Materials Genome database from LBNL. (Oct. 11) **Complete**
- (b) Map the electronic structure of Li<sub>x</sub>Ni<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>2</sub> as a function of Li content. (Oct. 11) **Complete**
- (c) Calculate the band structures of LiMnO<sub>2</sub> surfaces. (Dec. 11) **Delayed**
- (d) Predict the stable phases of the Li-graphene and Li-multi-graphene. (Feb. 12) **On schedule**
- (e) Complete the phase diagram of Li<sub>x</sub>Ni<sub>1/2</sub>Mn<sub>3/2</sub>O<sub>2</sub>. (Mar. 12) **On schedule**
- (f) Calculate the surface DOS of LiFePO<sub>4</sub> with different absorbents. (May 12) **On schedule**
- (g) Complete the kinetics of Li-graphene. (Sep. 12) **On schedule**

## PROGRESS TOWARD MILESTONES

**Collaborations:** Prof Gerbrand Ceder (MIT), Dr. Jordi Cabana (LBNL), Dr Robert Kostecki (LBNL), Dr Phil Ross (LBNL).

As part of the high-voltage spinel effort in the BATT Program, investigations have occurred on the cation ordering influence on the stable ground state, the electrochemical profile, and the Li diffusivity in  $\text{Li}_x(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$  as a function of Li content. Over 250 different Ni/Mn and Li/Vacancy arrangements have been calculated, and a coupled cluster expansion technique was applied to divulge the underlying cation interactions in the system and the preferred ground state arrangements. It was found that the Li and vacancies preferentially sit in ‘every-other-one’ zig-zag chains which will be maximally manifested at the half-lithiated state. However, these chains of Li-vacancies will only be stable if the nearest cation to each Li-Vac pair is a Ni, as depicted by the pink triangle in Fig. 1. In a uniformly disordered cation arrangement, this requirement can be fulfilled for every Li-Vac pair, which stabilizes the half-lithiated ground state and produces a voltage step at  $x = 0.5$ , as seen in experiments. For the ordered spinel, the requirement exhibited by the pink triangle in Fig. 1 is violated for a significant fraction of the Li-Vac pairs, which destabilizes the intermediate Li concentration states and the result is a lithiation process devoid of voltage steps. These results have recently been published in *Energy and Environmental Science*, 2012, DOI: 10.1039/C2EE03068C. The electronic structure of the material, as a function of Li content is being investigated to fulfill the remaining milestones.



**Figure 1.** The cation interactions in high-voltage Ni-Mn spinel. The preferred Li-Va zig-zag chains are shown with black lines and the Li-Va-cation triplet is displayed in pink. The unit cell displayed is the ordered spinel, and we highlight that the preferred Li-V-Ni arrangement is violated by the presence of a Mn cation (blue).

The work on the Mn spinel surfaces is almost complete. In the Mn spinel observed, in agreement with experimental results, a predominance of the (111) surface manifests in very regularly formed octahedra at equilibrium conditions.

The plan is to continue to develop and expand the large public database structure contained in the Materials Project ([www.materialsproject.org](http://www.materialsproject.org)). Currently we are displaying over 200 Li intercalation paths with multiple voltage profiles, energy density, capacity, oxygen release, and crystal structure information. We are working on developing a comparable Li conversion energy storage analysis. Since its launch in October 2011, The Materials Project has 1500 registered users, whereof approximately 25% are industry-affiliated.